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The Theory of Non-Newtonian Liquids

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1.

A *non-Newtonian liquid* is a liquid which does not conform to Newton's postulate, which states that in simple shear the shearing (or tangential) stress p_{nt} is proportional to the rate of shear (or tangential component of the velocity-deformation) $\dot{e}_{nt}$, on any plane whose normal is "n," i.e.,

$$\dot{e}_t = \varphi p_t, \qquad (1)^1$$

where φ is a mechanical material-constant called the *coefficient of fluidity*, and the dot is used to denote the time derivative. This Eq. (1) is called the rheological equation of state of the material. It is a basic law and can as such not be directly verified.[2] If, however, the differential Eq. (1) is integrated for the stationary flow through a tube with the radius R and the length l, the result is

$$Q/t = \varphi R^4 \pi p/8l, \qquad (2)$$

where Q is the quantity of liquid flowing through the tube during the time t under the pressure drop p/l. Eq. (2) is known as the Hagen[3]-Poiseuille law. If R and l are measured, and correlated values of Q/t and p are observed, φ can be calculated from

$$\varphi = 8Ql/R^4 \pi t p \qquad (3)$$

and is a constant[4] in the case of the Newtonian liquid if there is no "wall effect."[5] For a non-Newtonian liquid, however, which does not conform to Eq. (1) the quantity calculated according to (3) is not a constant and is then usually called the "*apparent fluidity*" φ'. (See Table I.)

TABLE I. *Apparent fluidity of a solution of crepe-rubber in toluene (1.77 percent conc. by weight).* Temperature 20°C.

p^* cm H_2O	t sec.	$10^3 Q/t$ cm³ sec.$^{-1}$	φ' rhes.
(a) Measured in a Bingham viscometer $R=0.0238$ cm $l=9.93$ cm $Q=5.98$ cm³			
− 86.4	3038.1	1.31	1.23
+131.5	1610.4	2.47	1.52
−181.0	1033.5	3.87	1.72
+224.6	728.8	5.47	1.97
−274.2	545.0	7.32	2.16
+316.8	425.0	9.38	2.39
−361.9	352.4	11.3	2.53
(b) Measured in a Bingham viscometer $R=0.0412$ cm $l=9.90$ cm $Q=4.00$ cm³			
+ 38.3	846.8	4.73	1.10
− 84.4	278.4	14.36	1.52
−132.3	142.4	28.1	1.90
−178.0	89.8	44.6	2.24
−225.6	62.4	64.2	2.53

* The pressure entered here is the reduced pressure after taking account of all necessary corrections. A positive pressure is applied on the "left" limb, a negative pressure on the "right."

This statement cannot be reversed; i.e., if a material is pressed through a tube and a coefficient calculated according to (3) turns out to be variable, this does not prove that the material is a non-Newtonian liquid. It has first been shown by Bingham[6] that a material for which the postulate

$$\dot{e}_t = \varphi(p_t - \theta) \qquad (4)$$

holds good, and which is a plastic solid with the yield value θ, also leads to a variable apparent

[1] The notation follows the system adopted in the author's *Introduction to Mathematical Rheology* and explained in J. Rheol. **3**, 264 (1932). Whenever there is no danger of ambiguity, we will, however, write p_t and e_t for p_{nt} and e_{nt}.

[2] M. Reiner, *Introduction to Mathematical Rheology.* (In press); Cf. J. Rheol. **3**, 245 (1932).

[3] E. Hagen, Pogg. Ann. **46**, 437 (1839) derived this law before Poiseuille.

[4] With respect to all quantities appearing in Eq. (3).

[5] With respect to the "wall-effect" see Sections 8 to 11.

[6] E. C. Bingham, Bur. Stand. Sci. Paps. **13**, 309 (1916).

fluidity, which is according to Buckingham[7] and Reiner[8]

$$\varphi' = \varphi[1-(4/3)(2\theta l/Rp)+(1/3)(2\theta l/Rp)^4]. \quad (5)$$

For the non-Newtonian liquid therefore the criterion that φ' is variable has to be amplified by the condition that θ vanishes.

2.

It is not possible to decide by appearance whether a given material which flows is a liquid or a very soft plastic solid. Every flow investigation has therefore to be expressed at the first stage in terms of *consistency* which concept can be applied to liquids and solids as well. In every rheological experiment an observed *kinematical quantity* (V) is related to an observed *dynamical quantity* (P). In the case of the Hagen-Poiseuille-experiment the kinematical quantity is Q/t and the dynamical quantity is p or p/l. In the case of the Margules[9]-Couette[10] experiment, V is the number of revolutions of the outer cylinder per unit time (n) and P the difference of the readings on the deflection scale (Δs). In both cases however other more convenient quantities can be substituted for the quantities just mentioned (see Section 6). If we plot the kinematical quantity as ordinate against the dynamical quantity as abscissa, the resultant curve is the "*consistency curve.*" (See Fig. 1.)

From an examination of the consistency curve it is sometimes possible to decide whether the material, under investigation, is a solid. If the consistency curve starts at a point on the P-axis, other than the origin, the material is a solid. This statement cannot be reversed. If the consistency curve passes through the origin, the material may be either a liquid or a solid which does not adhere to the wall of the apparatus, i.e., which shows *slippage* or generally a *wall-effect.*

It therefrom results that a theory of non-Newtonian liquids has to start from a general theory of flow of materials. At a later stage only (from Section 12 on) is it possible to branch off with a theory which is solely devoted to the flow of liquids.

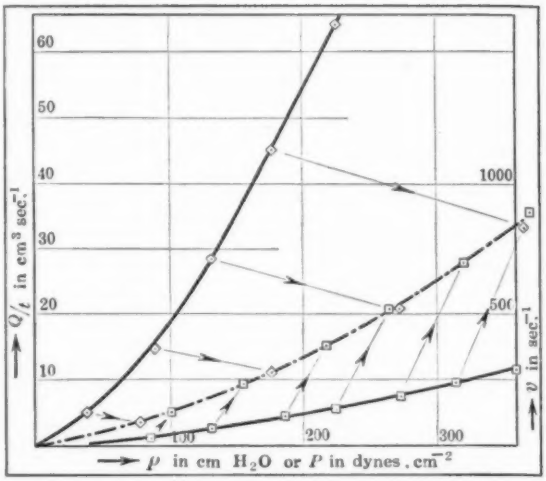

FIG. 1. Consistency curves of rubber-benzene solutions, the data for which are given in Table I (——— plotted as usual; — — — — — plotted in consistency variables).

3.

A very valuable contribution to the general theory of flow has recently been made by Hohenemser and Prager.[11] Every rheological equation of state is a relation between the tensors of stress and strain and their time derivatives. We confine ourselves here to homogeneous and isotropic or quasi-isotropic materials. We assume that the volumetric strain[12] depends only upon the hydrostatic pressure and that *vice versa* a hydrostatic pressure does not change the form of the body, i.e., does not produce *deformation.* For the case of deformation, we therefore have to consider such stresses only as are in excess of the hydrostatic pressure and such strains as are in excess of the volumetric strain. It can be shown by mathematical analysis that in every such deformed body, where the volume has not been changed, there exist at every point directions (n) for which the normal components of deformation (e_{nn}) vanish, i.e., where there is only pure shear in the plane-element, which is at right angles to n. Likewise there exist in every point plane-elements the stress across which is reduced to a pure shearing stress. For an isotropic body it can be assumed that the plane elements of pure shear and pure shearing stress are identical. With these assumptions, Hohenemser and

[7] E. Buckingham, Proc. Am. Soc. Test. Mat. **21**, 1 (1921).
[8] M. Reiner, Koll. Zeits. **39**, 80 (1926).
[9] M. Margules, Wien. Sitzungsber (2A) **83**, 588; **84**, 49 (1881) proposed the rotation-viscometer before Couette.
[10] M. Couette, Ann. de chim. **21**, 433 (1890).
[11] K. Hohenemser and W. Prager, Zeits. f. angew. Math. u. Mech. **11** (1931); cf. J. Rheol. **3**, 16 (1932).
[12] This is a strain which changes the volume only, but not the form of the body.

Prager have shown that if a relation between the *tangential components* of the stress and deformation and their time derivatives is assumed, the rheological equation of state of the body is completely determined; and they have also shown how the general three-dimensional differential equations, or the tensor relations, can be derived from the one-dimensional postulate about the tangential components. As a special case they have discussed the most general *linear* law of flow.[13] It is however obvious that *no* linear law of whatever form can adequately describe the flow-properties of a non-Newtonian liquid. A theory of non-Newtonian liquids can therefore only result from a *nonlinear* law of flow. Such a nonlinear law will be derived in the next section, with Hohenemser and Prager's system as a starting point.

4.

As has been explained in the previous section, the general rheological equation of state can be expressed by the formal equation

$$f(p_t, \dot{p}_t, e_t, \dot{e}_t) = 0. \tag{6}$$

We are here concerned with a *flowing* material. In this case, the quantity e_t cannot appear in the equation of state for the following reason: Flow is *continuous* deformation under a *constant* force. If the amount of shear is of influence on the state of stress in the material, this influence can only consist in increasing p_t with increasing On the other hand, deformation under the action of external forces can only continue until the internal stresses have increased to such an extent as to counterbalance the external forces. When this state has been reached, the deformation stops and consequently there is no flow. In a flowing material, which may be either a liquid or a plastic solid above the yield value, the amount of deformation is therefore not material but only the deformation *velocity*. This is tantamount to the stipulation that we do not consider strain-hardening.

For a flowing material Eq. (6) becomes accordingly:

$$f(p_t, \dot{p}_t, \dot{e}_t) = 0. \tag{7}$$

Eq. (7) can be further simplified if we consider *steady* flow only. This is the case with the Hagen-Poiseuille, and the Margules-Couette experiments which we may call the *fundamental* rheological experiments. If the flow is steady, the stresses are for obvious reasons functions of the space coordinates only, but not of the time. Therefore $\dot{p}_t$ vanishes and for stationary flow we have

$$f(p_t, \dot{e}_t) = 0. \tag{8}$$

This result is of importance for the following reasons: In Europe "viscosity anomalies" have first been observed in the case of liquids showing dynamic elasticity, i.e., elastic behavior against instantaneous stress.[14] This leads to explaining these anomalies as due to an "elasticity" of the material. This elasticity was then identified with the static elasticity of cohesional forces and a law of the same form as Bingham's law (4) assumed by Szegvari[15] and Reiner.[8] The law, Eq. (4), however, covers a *wider* range, as no assumption is introduced with regard to the origin of the yield value θ. The yield value may be due to cohesional forces showing elasticity; it may, however, also be due to other forces, as solid friction between suspended particles, surface tension, etc. As a matter of fact, Bingham had first, when proposing his equation, started from a concept of solid friction and called θ accordingly "the friction constant." It should now be remembered that the phenomenon of dynamic elasticity is connected with the occurrence of $\dot{p}_t$ in the differential equations of flow.[16] As it has just been proved that in the case of stationary flow $\dot{p}_t$ vanishes, this also proves that there is no direct connection between an observed dynamical elasticity of a material and its viscosity "anomaly" in either of the fundamental rheological experiments.

5.

Instead of Eq. (8), we can also write

$$\dot{e}_t = f(p_t). \tag{9}[17]$$

The function f can be developed into a Taylor-

[13] K. Hohenemser and W. Prager, J. Rheol. **3**, 16 (1932).

[14] W. R. Hess, Kolloid Zeits. **27**, 154 (1920) where reference is made to observations of 1906.

[15] A. Szegvari, Zeits. f. physik. Chemie **108**, 175 (1924).

[16] M. Reiner, J. Rheol. **3**, 253 (1932).

[17] Here f indicates, of course, a different relationship than f in Eq. (8).

series and the result is

$$\dot{e}_t = \sum_{n=1}^{n=\infty} \frac{1}{n!} \frac{df^{(n)}(\vartheta)}{dp_t^n} (p_t - \vartheta)^n. \tag{10}$$

In Eq. (10) we have an infinite number of coefficients $f^{(n)}(\theta)$. They are, however, all functions of a limited number of physical constants, which characterize the rheological behavior of the material. Eq. (10) is the general law of steady flow of any material. It was first derived by Reiner[18] without, however, noting the restriction that it holds good in the case of *steady* flow only.

The problem is now, given the general law of steady flow, Eq. (10), to find the corresponding V/P relation. The procedure is quite analogous to the one adopted by the author in a previous paper.[18] By introducing in the case of the

Hagen-Poiseuille Experiment

$$p_t = rp/2l, \qquad \dot{e}_t = -dv/dr,$$

where
p/l is the pressure drop,
l is the length of the capillary,
r is the distance of the layer from the axis of the cylinder,

Margules-Couette Experiment

$$p_t = (\tfrac{1}{2}\pi r^2)(M/l), \tag{11}$$

$$\dot{e}_t = r\,d\omega/dr, \tag{12}$$

where
M is the rotational moment,
l is the length of the inner cylinder,

we get

$$-\frac{dv}{dr} = \sum_{n=1}^{n=\infty} \frac{f^{(n)}(\vartheta)}{n!} \left(\frac{r}{2}\frac{p}{l} - \vartheta\right)^n, \qquad r\frac{d\omega}{dr} = \sum_{n=1}^{n=\infty} \frac{f^{(n)}(\vartheta)}{n!} \left(\frac{M}{2\pi r^2 l} - \vartheta\right)^n, \tag{13}$$

and through integration

$$v = \frac{2l}{p} \sum_{n=1}^{n=\infty} \frac{f^{(n)}(\vartheta)}{n!} \frac{(rp/2l - \vartheta)^{n+1}}{n+1} + k$$

for $p_t \geqq \vartheta$,
i.e., for $r \geqq r_0 = \dfrac{2\vartheta l}{p}$.

$$\omega = \sum_{n=1}^{n=\infty} \frac{f^{(n)}(\vartheta)\vartheta^n}{n!} \left\{ \sum_{m=0}^{m=n-1} \frac{(-1)^m}{2(m-n)} \binom{n}{m} \left(\frac{2\pi r^2 l\vartheta}{M}\right)^{n-m} + (-1)^n \ln r \right\} + k \tag{14}$$

for $p_t \geqq \vartheta$,
i.e., for $r \leqq r_0 = (M/2\pi l\vartheta)^{\frac{1}{2}}$. (15)

For the determination of the integration constant k it is usually assumed that the velocity of the flowing material in the layer adjacent to a solid wall is identical with the velocity of the wall. If this is the case we have

$$k = -\frac{2l}{p} \sum_{n=1}^{n=\infty} \frac{f^{(n)}(\vartheta)}{n!} \frac{(Rp/2l - \vartheta)^{n+1}}{n+1},$$

where R is the radius of the capillary,

$$k = -\sum_{n=1}^{n=\infty} \frac{f^{(n)}(\vartheta)\vartheta^n}{n!} \left\{ \sum_{m=0}^{m=n-1} \frac{(-1)^m}{2(m-n)} \binom{n}{m} \left(\frac{M}{2\pi R_1^2 l\vartheta}\right)^{n-m} + (-1)^n \ln R_1 \right\}, \tag{16}$$

where R_1 is the radius of the inner suspended cylinder,

and therefore

$$v = \frac{2l}{p} \sum_{n=1}^{n=\infty} \frac{f^{(n)}(\vartheta)}{n!} \frac{(Rp/2l - \vartheta)^{n+1} - (rp/2l - \vartheta)^{n+1}}{n+1}$$

for $r \geqq r_0$,

$$\omega = \sum_{n=1}^{n=\infty} \frac{f^{(n)}(\vartheta)\vartheta^n}{n!} \left\{ \sum_{m=0}^{m=n-1} \frac{(-1)^m}{2(n-m)} \binom{n}{m} \left(\frac{M}{2\pi l\vartheta}\right)^{n-m} \times [R_1^{2(m-n)} - r^{2(m-n)}] + (-1)^n \ln (r/R_1) \right\} \tag{17}$$

for $r \leqq r_0$,

[18] M. Reiner, [a] J. Rheol. **1**, 11 (1929); [b] **1**, 250 (1930); [c] **1**, 5 (1929).

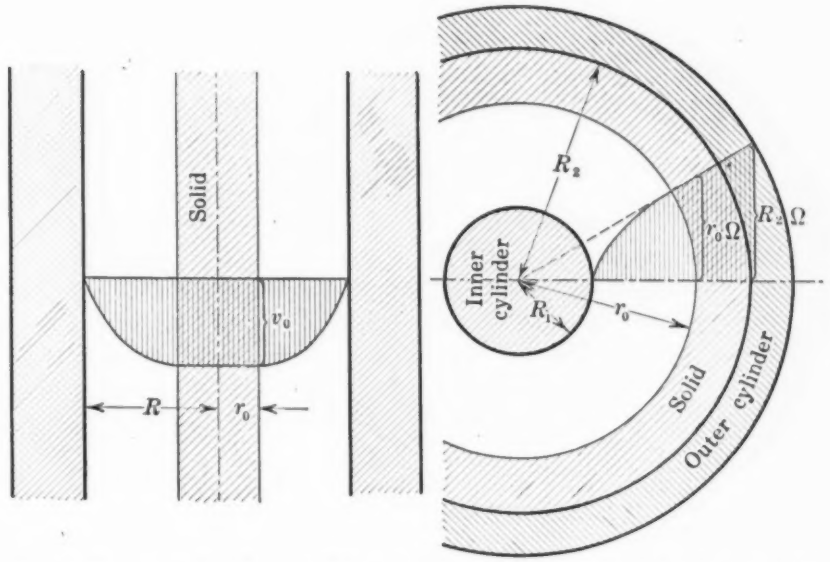

FIG. 2. Corresponding flow conditions in capillary tube and rotation instruments.

while for

$r \leqq r_0$ $\qquad$ $r \geqq r_0$

we have

$$v = v_0 = \frac{2l}{p} \sum_{n=1}^{n=\infty} \frac{f^{(n)}(\vartheta)}{n!} \frac{(Rp/2l - \vartheta)^{n+1}}{n+1} \cdot$$

$$\omega = \omega_0 = \sum_{n=1}^{n=\infty} \frac{f^{(n)}(\vartheta)\vartheta^n}{n!} \left\{ \sum_{m=0}^{m=n-1} \frac{(-1)^m}{2(n-m)} \times \left[\left(\frac{M}{2\pi R_1^3 l \vartheta} \right)^{n-m} - 1 \right] + (-1)^n \ln \left(\frac{M}{2\pi R_1^3 l \vartheta} \right)^{\frac{1}{2}} \right\} \cdot \quad (18)$$

See Fig. 2.

The volume of flow is therefore

$$Q/t = r_0^2 \pi v_0 + 2\pi \int_{r=r_0}^{r=R} v r dr$$

$$= \frac{8\pi l^3}{p^3} \sum_{n=1}^{n=\infty} \frac{f^{(n)}(\vartheta)}{(n+3)!} (Rp/2l - \vartheta)^{n+1} \times [(Rp/2l)^2 (n+1)(n+2) + (Rp\vartheta/l)(n+1) + 2\vartheta^2].$$

The angular velocity of the outer cylinder with the radius R_2 is therefore

$$\Omega = \sum_{n=1}^{n=\infty} \frac{f^{(n)}(\vartheta)\vartheta^n}{n!} \left\{ \sum_{m=0}^{m=n-1} \frac{(-1)^m}{2(n-m)} \binom{n}{m} \left(\frac{M}{2\pi l \vartheta} \right)^{n-m} \times [R_1^{2(m-n)} - R_2^{2(m-n)}] + (-1)^n \ln R_2/R_1 \right\} \quad (19)$$

for $M \geqq 2\pi l \vartheta R_2^2$;

and

$$\Omega = \sum_{n=1}^{n=\infty} \frac{f^{(n)}(\vartheta)\vartheta^n}{n!} \left\{ \sum_{m=0}^{m=n-1} \frac{(-1)^m}{2(n-m)} \left[\left(\frac{M}{2\pi l \vartheta R_1^2} \right)^{n-m} - 1 \right] + (-1)^n \ln \left(\frac{M}{2\pi l \vartheta R_1^2} \right)^{\frac{1}{2}} \right\} \quad (19')$$

for $M \leqq 2\pi l \vartheta R_2^2$.

Eqs. (19) express the general V/P or consistency relations for both fundamental rheological experiments. This solves the problem which we put before ourselves in the beginning of this section. If the Eq. (10) is given, we know all the coefficients $f'(\vartheta), f''(\vartheta) \cdots f^{(n)}(\vartheta)$. We therefore also know the coefficients of the power series Eqs. (19) and (19'). Conversely, if the consistency relations are empirically given through observation and the consistency curves can be analyzed, so that they can be expressed through power series of known coefficients, this leads to the establishment of the general

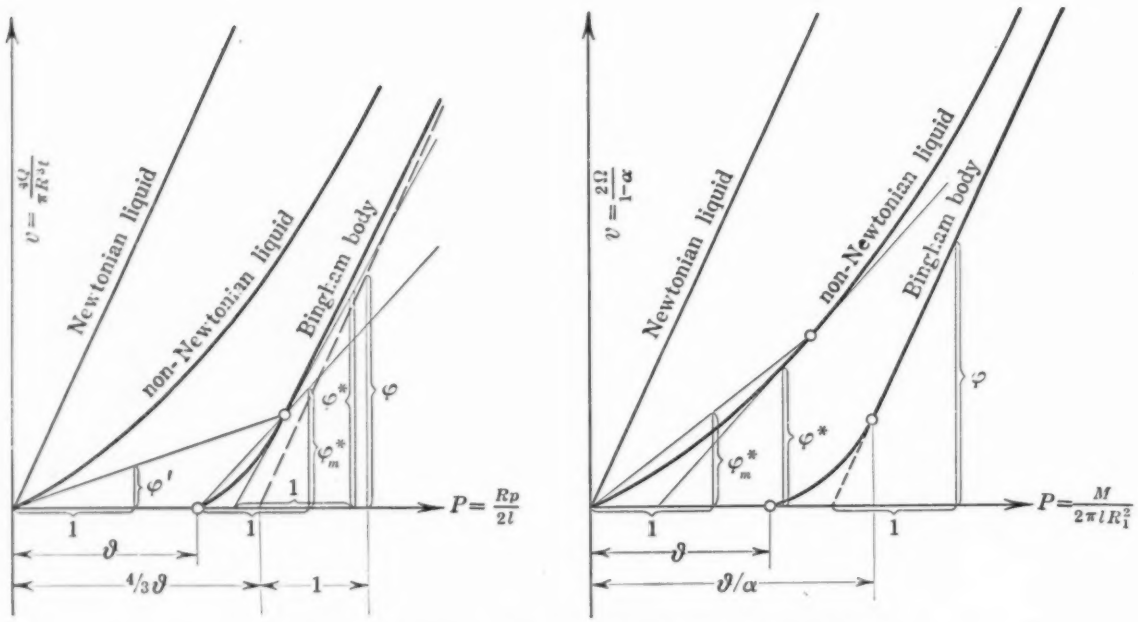

FIG. 3. Consistency curves for three types of material.

law of steady flow, Eq. (10), for the material under investigation. As will be shown later (Section 14) this method is however very limited in its possible applications.

If we specialize Eqs. (19) and (19′) for $n=0$, we get the equations for the non-Newtonian liquid; if we specialize for $n=1$ we get the equations for the Bingham body; if we specialize for $\vartheta=0$ and $n=0$ we get the Hagen-Poiseuille and the Margules-Couette laws, respectively.

6.

In the form just given, the consistency curves are not independent of the dimensions of the apparatus. (Compare Fig. 1.) It should however be noted that neither is this the case with, e.g., the $Q/t : p/l$ relation of the Hagen-Poiseuille law. General considerations of similitude lead us to expect that it should be possible to select such expressions for the V/P variables that the consistency curves for the same material and similar apparatus will be independent of the dimensions of the apparatus *irrespective* of the laws of flow and also of whether the material is a *liquid or a solid.*

An examination of Eqs. (19) together with expressions (11) shows that if we plot

$$V'=4Q/\pi R^3 t \qquad V=2\Omega/(1-\alpha),\quad \alpha=(R_1/R_2)^2 \tag{20}$$

against the shearing stress at the wall

$$P'=Rp/2l \qquad P'=M/2\pi l R_1^2, \tag{21}$$

we have in

$$V'=\frac{1}{P'}\sum_{n=1}^{n=\infty}\frac{4f^{(n)}(\vartheta)}{(n+3)!}(P'-\vartheta)^{n+1}[(n+1)(n+2)+2(n+1)\vartheta/P'+2(\vartheta/P')^2] \quad \text{for } P\geqq\vartheta$$

$$V'=\frac{1}{1-\alpha}\sum_{n=1}^{n=\infty}\frac{f^{(n)}(\vartheta)\vartheta^n}{n!}\left\{\sum_{m=0}^{m=n-1}\frac{(-1)^m}{n-m}\binom{n}{m}\times(P/\vartheta)^{n-m}[1-\alpha^{n-m}]-(-1)^n\ln\alpha\right\} \quad \text{for } P'\geqq\vartheta/\alpha \tag{22}$$

and

$$V'=0 \quad \text{for} \quad P' \leqq \vartheta,$$

$$V'=\frac{1}{1-\alpha}\sum_{n=1}^{n=\infty}\frac{f^{(n)}(\vartheta)\vartheta^n}{n!}\left\{\sum_{m=0}^{m=n-1}\frac{(-1)^m}{n-m}\binom{n}{m}\times[(P'/\vartheta)^{n-m}-1]+(-1)^n \ln P'/\vartheta\right\} \quad (22')$$

for $P' \geqq \vartheta/\alpha$

and $V'=0 \quad \text{for} \quad P' \leqq \vartheta,$

expressions which are independent of the dimensions of geometrically similar apparatus.[19] (See Fig. 1.) Such a demonstration as given here for the fundamental rheological experiments is always possible and no other V/P variables should herefore be used in plotting consistency curves. For this reason, the concept "consistency curve" will be used so as to mean the curve when plotted in such a way as to be independent of the dimensions of the apparatus and we will write V and P for V' and P'. (See Fig. 3.)

7.

The apparent fluidity can be calculated from expressions (22). We get

$$\varphi'=\frac{8Ql}{\pi R^4 p}=\frac{V}{P}=\frac{1}{P^2}\sum_{n=1}^{n=\infty}\cdots \qquad \varphi'=\frac{4\pi l\Omega}{M(1/R_1^2-1/R_2^2)}=V/P=\frac{1}{(1-\alpha)P}\sum_{n=1}^{n=\infty}\cdots \quad (23)$$

for $P \geqq \vartheta$

and $\varphi'=0$

for $P \leqq \vartheta.$

for $P \geqq \vartheta/\alpha$

and $\varphi'=\dfrac{1}{(1-\alpha)P}\sum_{n=1}^{n=\infty}\cdots \quad (23')$

for $P \leqq \vartheta/\alpha$

and $\varphi'=0 \quad \text{for} \quad P \leqq \vartheta. \quad (23'')$

If we plot the apparent fluidity against the shearing stress at the wall, the resultant curves are therefore also independent of the dimensions of the apparatus.

If we now examine the equations of state (1) for the Newtonian liquid and (4) for the Bingham-body, it can be seen that the quotient $\dot{e}_i/p_i$ gives the fluidity φ in the first case, but not in the second case. In the second case we get

$$\dot{e}_i/p_i=\varphi(1-\vartheta/p_i), \quad (24)$$

and this is the apparent fluidity for the plane two-dimensional case. (See Fig. 4.) The fluidity can therefore generally not be defined by the quotient of the rate of shear to shearing stress and different definitions have to be used in the case of the fluid and the solid for a magnitude which is of the same nature. For this reason also a different name, "mobility," was introduced by Bingham in the case of a solid for what is "fluidity" in the case of a liquid.

If, however, we define φ by

$$\varphi=d\dot{e}_i/dp_i \quad (25)[20]$$

we get in both cases, i.e., from either Eq. (1) or (4) $d\dot{e}_i/dp_i=\varphi$. We are then justified in using *one* term only, i.e., the term fluidity. In analogy to the expressions (25) we define by

$$\varphi^*=dV/dP \quad (26)$$

the *practical* fluidity φ^*, where V and P are such kinematical and dynamical quantities as make the consistency curve independent of the dimensions of the apparatus.

The usefulness of this new concept will be seen from the following: Suppose we are making flow experiments with a material of which we do not know whether it is a liquid or a plastic solid, we

[19] For the tube this qualification is not necessary, for the rotation instrument however this implies that α is constant.

[20] Compare with the usual nomenclature, e.g., Mooney, J. Rheol. **2**, 215 (1931). (Editor.)

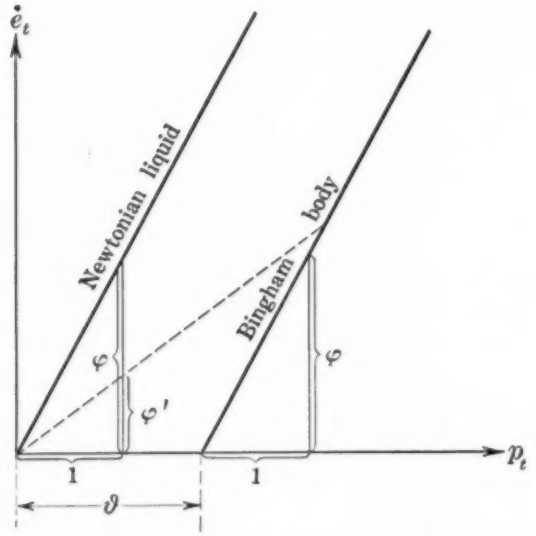

FIG. 4. True and apparent fluidity of the Bingham body.

measure related values for

$$Q/t \quad \text{and} \quad p/l \qquad\qquad \Omega \quad \text{and} \quad M$$

calculate

$$V=4Q/\pi R^3 t \quad \text{and} \quad P=Rp/2l \qquad\qquad V=2\Omega/(1-\alpha) \quad \text{and} \quad P=M/2\pi R_1^2 l$$

from the known dimensions of the apparatus[21] and plot V against P. From this curve, we determine graphically (or by some other suitable method) φ^* and plot it against P. This curve then represents the functional relationships:

$$\varphi^*=\frac{1}{P}\sum_{n=1}^{n=\infty}\frac{4f^{(n)}(\vartheta)}{(n+3)!}(P-\vartheta)^n\{n(n+1)(n+2)+3n(n+1)\vartheta/P+6n(\vartheta/P)^2+6(\vartheta/P)^3\}$$

for $P\geqq\vartheta$

and $\varphi^*=0$

for $P\leqq\vartheta$.

$$\varphi^*=\frac{1}{1-\alpha}\sum_{n=1}^{n=\infty}\frac{f^{(n)}(\vartheta)}{n!P}[(P-\vartheta)^n-(P\alpha-\vartheta)^n] \qquad (27)^{22}$$

for $P\geqq\vartheta/\alpha$

and $$\varphi^*=\frac{1}{1-\alpha}\sum_{n=1}^{n=\infty}\frac{f^{(n)}(\vartheta)}{n!P}(P-\vartheta)^n \qquad (27')$$

for $P\leqq\vartheta/\alpha$,

and $\varphi^*=0$ (27″)

for $P\leqq\vartheta$.

For the Newtonian liquid, i.e., $n=1$, $\vartheta=0$, specialization of the Eq. (27) gives in both cases

$$\varphi^*=f'(0)=\varphi.$$

For the Bingham-body, i.e., $n=1$, we get

$$\varphi^*=f'(\vartheta)[1-(\vartheta/P)^4]=\varphi[1-(\vartheta/P)^4]$$

for $P\geqq\vartheta$,

which for large values of P can be put as equal to φ,

$$\varphi^*=f'(\vartheta)=\varphi \quad \text{for} \quad P\geqq\vartheta/\alpha \qquad (28)$$

and $$\varphi^*=\frac{f'(\vartheta)}{1-\alpha}(1-\vartheta/P)=[\varphi/(1-\alpha)][(1-\vartheta)/P] \qquad (28')$$

for $P\leqq\vartheta/\alpha$.

[21] Instead of determining directly the dimensions of the apparatus, we can of course calibrate it with a liquid of known constants.

[22] After differentiation of the expressions on the right side, Eqs. (22) and (22′), the m-summation can be carried out.

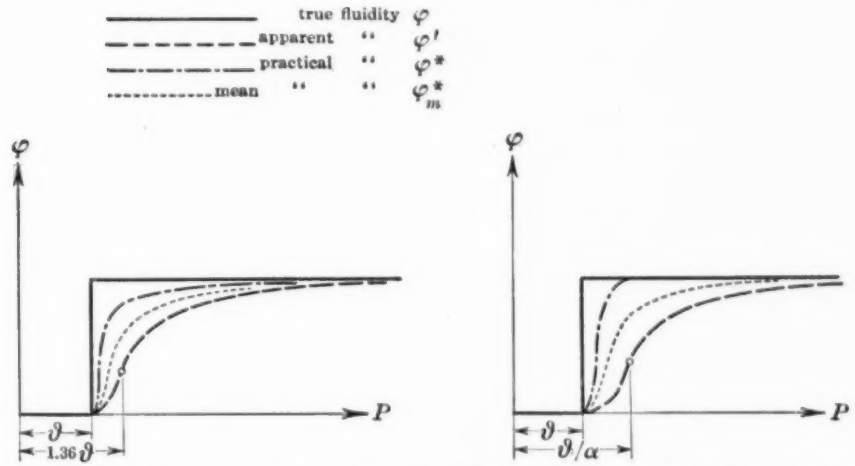

FIG. 5. True, apparent, practical, and mean practical fluidity of the Bingham body.

while for $P \leqq \vartheta$, we have $\varphi^* = 0$ in both cases. The practical fluidity therefore has a very close relation to the true fluidity; as a matter of fact, both are for all practical purposes identical. In Fig. 5, the true fluidity, the practical fluidity and the apparent fluidity are shown and the advantage of using the practical fluidity is obvious. Besides the true and the practical fluidity, the following quantity is of interest:

$$\varphi_m = \dot{e}_t/(p_t - \vartheta). \tag{29}$$

We may call it *the mean fluidity*. This designation suggests itself from an inspection of Fig. 5. The mean fluidity φ_m for the point $(p_t, \dot{e}_t)$ is identical with the true fluidity φ of a point between (0, 0) and $(p_t, \dot{e}_t)$. In the case of a liquid ϑ vanishes and the apparent fluidity φ' is identical with φ_m. We will accordingly use the following terminology. The apparent fluidity

$$\varphi' = \frac{\dot{e}_t}{p_t} \text{ i.e. } \frac{\text{rate of shear}}{\text{shearing stress}} \qquad \text{or} \qquad \frac{V}{P}, \text{ i.e., } \frac{\text{kinematical consistency variable}}{\text{dynamical consistency variable}}.$$

The apparent fluidity will only be used if it is not known whether the material is a solid or a liquid, or in case it is a liquid showing a "wall-effect."

$$\begin{aligned} \text{True fluidity } & \varphi = d\dot{e}_t/dp_t, \\ \text{mean fluidity } & \varphi_m = \dot{e}_t/(p_t - \vartheta), \\ \text{practical fluidity } & \varphi^* = dV/dP, \\ \text{mean practical fluidity } & \varphi_m^* = V/(P - P_0), \end{aligned}$$

where P_0 is the dynamical quantity corresponding to the yield value or the abscissa of the "yield point."

Besides these quantities it is sometimes advantageous to use another quantity, which, without being a "fluidity" is very closely related to it. Reynolds has introduced the plotting of flow-curves on a logarithmic scale. If we put

$$V_l = \log V, \qquad P_l = \log P \tag{30}$$

the $V_l : P_l$ curve is the *logarithmic homologue* of the consistency curve. We can then define by

$$\varphi_l = dV_l/dP_l \tag{31}$$

the *logarithmic fluidity*. The usefulness of this concept will be shown later.

8.

From Eq. (27) we find that generally φ^* vanishes for $P=\vartheta$. This could therefore furnish a criterion whether a given material is a liquid or a solid. As has, however, been remarked in Section 2 this criterion holds good only where there is no "slippage" or generally no "wall-effect."

As Bingham has pointed out, it is "quite possible that the fluidity of a liquid near the surface (solid wall) is not identical with that within the body of the liquid." [23] This gives rise to a wall-effect. However, even if the material does not wet the solid wall, one cannot properly speak of slippage in the sense in which this word is ordinarily used. In this case, there exists, according to Bingham,[23] a layer of some other medium, usually air, between the material and the solid wall. In the case of a soft solid, which consists of a liquid and a solid phase, as e.g., an oil-paint consists of the liquid vehicle and the solid pigment, a wall layer of pure liquid has to be assumed to be present between the wall of the apparatus and the flowing solid (e.g., the oil-paint).

We have therefore to generalize our equations to include such cases. Let us denote the thickness of the wall layer by d and its fluidity by φ_w. We assume φ_w to be constant, i.e., the wall layer is a Newtonian liquid.

The wall layer adheres to the wall.[24] We therefore have

$$V=\varphi_w(p/4l)(R^2-r^2)$$

for the layer near the wall.

$$\omega=\varphi_w(M/2\pi l)(1/R_1^2-1/r^2) \tag{32}$$

for the layer near the inner cylinder, and

$$\omega=\varphi_w(M/2\pi l)(1/r^2-1/R_2^2) \tag{32'}$$

for the layer near the outer cylinder.

These equations follow from Eqs. (17) for $\vartheta=0$, $n=1$. The velocity at the interface of the wall layer with the body of the liquid is

$$d=\varphi_w(p/4l)[R^2-(R-d)^2].$$

$$\omega_{d_1}=\varphi_w\frac{M}{2\pi l}\left(\frac{1}{R_1^2}-\frac{1}{(R_1+d)^2}\right), \tag{33}$$

$$\omega_{d_2}=\varphi_w\frac{M}{2\pi l}\left(\frac{1}{(R_2-d)^2}-\frac{1}{R_2^2}\right). \tag{33'}$$

(See Fig. 6.) We now have to go back to Eqs. (14) and to determine the integration constant so that

$$-d=\frac{2l}{p}\sum_{n=1}^{n=\infty}\frac{f^{(n)}(\vartheta)}{n!}\frac{[(R-d)p/2l-\vartheta]^{n+1}}{n+1}+k.$$

$$\omega_{d_1}=\sum_{n=1}^{n=\infty}\frac{f^{(n)}(\vartheta)\vartheta^n}{n!}\left\{\sum_{m=0}^{m=n-1}\frac{(-1)^m}{2(m-n)}\binom{n}{m}\times\left(\frac{M}{2\pi(R_1+d)^2l\vartheta}\right)^{n-m}+(-1)^n\ln(R_1+d)\right\}+k. \tag{34}$$

Introducing these integration constants into Eqs. (14) we get the following equations instead of Eqs. (17)

$$v=\frac{2l}{p}\sum_{n=1}^{n=\infty}\frac{f^{(n)}(\vartheta)}{n!}\frac{[(R-d)p/2l-\vartheta]^{n+1}-[rp/2l-\vartheta]^{n+1}}{n+1}+\varphi_w\frac{p}{4l}[R^2-(R-d)^2]$$

for $(R-d)\geqq r\geqq r_0=2\vartheta l/p.$

$$\omega=\sum_{n=1}^{n=\infty}\frac{f^{(n)}(\vartheta)\vartheta^n}{n!}\left\{\sum_{m=0}^{m=n-1}\frac{(-1)^m}{2(n-m)}\binom{n}{m}\left(\frac{M}{2\pi l\vartheta}\right)^{n-m}\times\left[\frac{1}{(R_1+d)^{2(n-m)}}-\frac{1}{r^{2(n-m)}}\right]+(-1)^n\ln\frac{r}{R_1+d}\right\}+\varphi_w\frac{M}{2\pi l}\left(\frac{1}{R_1^2}-\frac{1}{(R_1+d)^2}\right) \tag{35}$$

for $(R_1+d)\leqq r\leqq r_0=(M/2\pi l\vartheta)^{\frac{1}{2}}.$

Furthermore there is

$$v_w=\varphi_w(p/4l)(R^2-r^2)$$

for $R\geqq r\geqq(R-d)$

$$\omega_w=\varphi_w(M/2\pi l)(1/R_1^2-1/r^2) \tag{35'}$$

for $R_1\leqq r\leqq(R_1+d)$

[23] E. C. Bingham, *Fluidity and Plasticity.*

[24] M. Reiner, Zeits. f. Physik **79**, 139 (1932).

and

$$v=v_0=\frac{2l}{p}\sum_{n=1}^{n=\infty}\frac{f^{(n)}(\vartheta)}{n!}\cdot\frac{[(R-d)p/2l-\vartheta]^{n+1}}{n+1}+\varphi_w\frac{p}{4l}[R^2-(R-d)^2]$$

for $r\leqq r_0$.

$$\omega=\omega_0=\sum_{n=1}^{n=\infty}\frac{f^{(n)}(\vartheta)\vartheta^n}{n!}\left\{\sum_{m=0}^{m=n-1}\frac{(-1)^m}{2(n-m)}\binom{n}{m}\times\left[\left(\frac{M}{2\pi(R_1+d)^2l\vartheta}\right)^{n-m}-1\right]+(-1)^n\ln\left(\frac{M}{2\pi(R_1+d)^2l\vartheta}\right)^{\frac{1}{2}}\right\}+\varphi_w\frac{M}{2\pi l}\left(\frac{1}{R_1^2}-\frac{1}{(R_1+d)^2}\right)\quad(35'')$$

for $r\geqq r_0$.

This gives

$$V=\sum_{n=1}^{n=\infty}\frac{4f^{(n)}(\vartheta)}{(n+3)!}P^n\left\{\left[1-\frac{d}{R}-\frac{\vartheta}{P}\right]^{n+1}\left[\left(1-\frac{d}{R}\right)^2\frac{\vartheta}{R}+2\left(\frac{\vartheta}{P}\right)^2\right]\right\}+P\varphi_w\left[1-\left(1-\frac{d}{R}\right)^4\right]$$

for $P\geqq\vartheta/(1-d/R)$,

and $V=P\varphi_w[1-(1-d/R)^4]$

for $P\leqq\vartheta/(1-d/R)$.

$$V=\frac{1}{1-\alpha}\sum_{n=1}^{n=\infty}\frac{f^{(n)}(\vartheta)\vartheta^n}{n!}\left\{\sum_{m=0}^{m=n-1}\frac{(-1)^m}{n-m}\binom{n}{m}\left(\frac{P}{\vartheta}\right)^{n-m}\times\left[\frac{1}{(1+d/R_1)^{2(n-m)}}-\frac{\alpha^{n-m}}{(1-d/R_2)^{2(n-m)}}\right]+(-1)^n\ln\frac{1}{\alpha}\left(\frac{1-d/R_2}{1+d/R_1}\right)^2\right\}+2\varphi_wP\left[1-\frac{1-2d/(R_2-R_1)}{(1+d/R_1)^2(1-d/R_2)^2}\right]\quad(36)$$

for $P\geqq\vartheta/\alpha$,

and

$$V=\frac{1}{1-\alpha}\sum_{n=1}^{n=\infty}\frac{f^{(n)}(\vartheta)\vartheta^n}{n!}\left\{\sum_{m=0}^{m=n-1}\frac{(-1)^m}{n-m}\binom{n}{m}\times\left[\left(\frac{P/\vartheta}{(1+d/R_1)^2}\right)^{n-m}-1\right]+(-1)^n\ln\frac{P/\vartheta}{(1+d/R_1)^2}\right\}+2\varphi_wP\left[1-\frac{1-2d/(R_2-R_1)}{(1+d/R_1)^2(1-d/R_2)^2}\right]\quad(36')$$

for $P\leqq\vartheta/\alpha$,

and

$$V=2\varphi_wP\left[1-\frac{1-2d/(R_2-R_1)}{(1+d/R_1)^2(1-d/R_2)^2}\right]\quad(36'')$$

for $P\geqq\vartheta(1+d/R_1)^2$.

From Eqs. (36), (36′) and (36″) it follows that whenever there exists a "wall-effect," the consistency-curve is *not independent of the dimensions of the apparatus* and furthermore that, if the material is a plastic solid, the consistency curve starts with a straight line. The second part of this statement cannot be reversed, i.e., if the consistency curve starts with a straight line, the material may either be a plastic solid with a wall-effect or a liquid with or without a wall-effect.

9.

Expressions for the fluidities in case where there exist wall-effects can be easily derived from Eqs. (36) and (36′). For the Newtonian liquid, i.e., $n=1$, $\vartheta=0$, specialization of the resultant expressions gives

$$\varphi^*=\varphi_w-(\varphi_w-\varphi)(1-d/R)^4.\qquad\varphi^*=2\varphi_w-(2\varphi_w-\varphi)\frac{1-2d/(R_2-R_1)}{(1+d/R_1)^2(1-d/R_2)^2}.\quad(37)$$

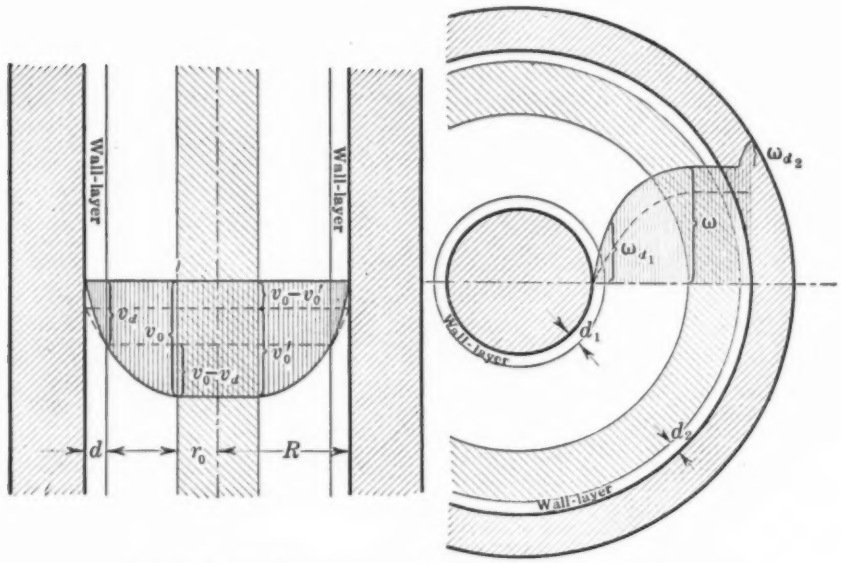

FIG. 6. Plastic flow in the case where there exist wall-layers.

For the Bingham-body, i.e., $n=1$, we get

$$\varphi^*=\varphi_w-(\varphi_w-\varphi)(1-d/R)^4-\varphi(\vartheta/P)^4$$

for $P\geqq\vartheta/(1-d/R)$,

and

$$\varphi^*=\varphi_w[1-(1-d/R)^4]$$

for $\vartheta/(1-d/R)$.

$$\varphi^*=2\varphi_w-(2\varphi_w-\varphi)\frac{1-2d/(R_2-R_1)}{(1+d/R_1)^2(1-d/R_2)^2} \tag{38}$$

for $P\geqq\vartheta/\alpha$

and

$$\varphi^*=2\varphi_w\left[1-\frac{1-2d/(R_2-R_1)}{(1+d/R_1)^2(1-d/R_2)^2}\right]+\frac{1}{1-\alpha}\varphi\left[\frac{1}{(1+d/R_1)^2}-\frac{\vartheta}{P}\right] \tag{38'}$$

for $P\leqq\vartheta/\alpha$,

and

$$\varphi^*=2\varphi_w\left[1-\frac{1-2d/(R_2-R_1)}{(1+d/R_1)^2(1-d/R_2)^2}\right] \tag{38''}$$

for $P\leqq\vartheta(1+d/R_1)^2$.

For the non-Newtonian liquid, i.e., $\vartheta=0$, we get

$$\varphi^*=\varphi_w-\left\{\varphi_w-\sum_{n=1}^{n=\infty}\frac{4f^{(n)}(0)}{n+3}\frac{[P(1-d/R)]^{n-1}}{(n-1)!}\right\}(1-d/R)^4.$$

$$\varphi^*=2\varphi_w\left[1-\frac{1-2d/(R_2-R_1)}{(1+d/R_1)^2(1-d/R_2)^2}\right]+\frac{1}{1-\alpha}\sum_{n=1}^{n=\infty}\frac{f^{(n)}(0)P^{n-1}}{n!}\left[\frac{1}{(1+d/R_1)^{2n}}-\frac{\alpha^n}{(1-d/R_2)^{2n}}\right]. \tag{39}$$

10.

It was stated in Section 2 that if the consistency curve of a material starts from a point on the P-axis with a finite abscissa, this proves that the material is a solid. We are now in the position to amplify this criterion for the case where the consistency-curve passes through the origin. In this case one has first to determine the practical fluidity at rest, i.e., for $P=0$. If the material is a plastic solid this is

$$\varphi_0^*=\varphi_w[1-(1-d/R)^4].\qquad \varphi_0^*=2\varphi_w\left[1-\frac{1-2d/(R_2-R_1)}{(1+d/R_1)^2(1-d/R_2)^2}\right]. \tag{40}$$

If however it is a liquid we have

$$\varphi_0^*=\varphi_0+\varphi_w[\cdots].\qquad \varphi_0^*=\varphi_0+2\varphi_w[\cdots]. \tag{41}$$

If we now vary the dimensions of the apparatus, i.e.,

the radius	R	the radii R_1 and R_2, keeping α constant

and plot the calculated values against

$1/R$	$1/R_1$

then extrapolation of this curve for

$1/R=0$	$1/R_1=0$

gives $\varphi_0^*=0$ in the case of a plastic solid and $\varphi_0^*=\varphi_0\neq 0$ in the case of a (Newtonian or non-Newtonian) liquid.

This provides us with a definite criterion of whether a material is a plastic solid or a liquid. As we are not, in the present paper, concerned with the flow of solids, we will assume in our further investigations that $\vartheta=0$, i.e., in the general case of a wall effect we have

$$V=P\varphi_w[1-(1-d/R^4)]+\sum_{n=1}^{n=\infty}\frac{4f^{(n)}(0)}{(n+3)!}P^n(n+1)(n+2)(1-d/R)^{n+3} \qquad V=2P\varphi_w\left[1-\frac{1-2d/(R_2-R_1)}{(1+d/R_1)^2(1-d/R_2)^2}\right]+\frac{1}{1-\alpha}\sum_{n=1}^{n=\infty}\frac{f^{(n)}(0)}{n!}\frac{P^n}{n}\left[\frac{1}{(1+d/R_1)^{2n}}-\frac{\alpha^n}{(1-d/R_2)^{2n}}\right] \quad (42)$$

and where there is no wall-effect we have

$$V=\sum_{n=1}^{n=\infty}\frac{4f^{(n)}(0)}{(n+3)!}P^n(n+1)(n+2). \qquad V=\frac{1}{1-\alpha}\sum_{n=1}^{n=\infty}\frac{f^{(n)}(0)}{n!}\frac{P^n}{n}(1-\alpha^n). \quad (43)$$

These consistency curves correspond to a rheological equation of state of a non-Newtonian liquid

$$\dot{e}_t=f(p_t)=\sum_{n=1}^{n=\infty}\frac{f^{(n)}(0)}{n!}p_t^n. \quad (44)$$

11.

The wall-effect can be considered under two aspects. It may be of interest to determine the thickness of the wall layer and its fluidity. In order to accomplish this, we differentiate Eqs. (41) in respect of

$1/R$	$1/R_1$ remembering that R_1/R_2 is a constant.

We get

$$d\varphi_0^*/d(1/R)=4\varphi_w d(1-d/R)^3. \qquad d\varphi_0^*/d(1/R_1)=4\varphi_w d\cdot\frac{(1+d/R_1)(1-d/R_2)+R_2/R_1-1-2d/R_1}{(R_2/R_1-1)(1+d/R_1)^3(1-d/R_2)^3}. \quad (45)$$

Extrapolating the curve defined by (45) for $1/R=0$ we get in both cases

$$[d\varphi_0^*/d(1/R)]_0=4\varphi_w d. \quad (46)$$

If φ_w is known this gives the thickness of the wall layer. Otherwise, a further differentiation and extrapolation furnishes another value so that both unknowns φ_w and d can be calculated.

If, however, the problem is to determine the consistency of the *body* of the material, the wall-effect is bothersome and has to be eliminated by means of correction. This can be done as follows: One has first to determine the true fluidity of the material at rest φ_0 as explained in Section 10. If we know this, we redraw the consistency curve for a coordinate system as shown in Fig. 1. The

consistency curve in respect to the new V/P coordinate system is given by the following equations:

$$\frac{[V-P(\varphi_0^*-\varphi_0)]\varphi_w}{\varphi_w+\varphi_0-\varphi_0^*} = \sum_{n=1}^{n=\infty} \frac{4f^{(n)}(0)}{(n+3)!} P^n(n+1)(n+2)(1-d/R)^{n-1}.$$

$$\frac{[V-P(\varphi_0^*-\varphi_0)]2\varphi_w}{2\varphi_w+\varphi_0-\varphi_0^*} = \sum_{n=1}^{n=\infty} \frac{f^{(n)}(0)}{n!} \frac{P^n}{n} \frac{[(1-d/R_2)^{2n}-\alpha^n(1+d/R_1)^{2n}]}{[(1-d/R_2)^2-\alpha(1+d/R_1)^2]} \cdot \frac{1}{(1+d/R_1)^{2(n-1)}(1-d/R_2)^{2(n-1)}}. \quad (47)$$

The first term of the series, i.e., for $n=1$, is $f'(0)\cdot P$ and is identical with the first term of a liquid showing no wall-effect. In the case of a Newtonian liquid showing a wall-effect this curve is therefore the correct consistency curve of the bulk of the material. We may therefore call the consistency curve as given by Eq. (45) the "bulk"-consistency curve. It is identical with the consistency curve of the bulk of a non-Newtonian liquid showing a wall-effect, if either small P's are considered or d/R is small. For larger P's and larger d/R's there is no way of plotting consistency curves independently of the dimensions of the apparatus, if the law of flow of the material is not known.

12.

The foregoing investigations have furnished us (a) with a criterion with which to decide from observations whether a material, the law of flow of which is not known, is a solid or a liquid, and (b) with a method of how to plot the observations so that the curve is entirely independent of the dimensions of the apparatus, where there is no wall-effect, or is approximately independent of the dimensions, where there is a wall-effect.

It is, however, not possible to plot the consistency curve in such a way that observations made with the same material in *different sort of apparatus* (e.g., capillary and rotation) will give the same curve, if the law of flow of the material is not known. The only advantage, at this stage, of having made observations with a different sort of apparatus is this, that the different consistency curves have the same shape near the origin or all extrapolate to the same practical fluidity at rest, which is identical with the true fluidity at rest. It is therefore possible to compare the measurements made with different sorts of apparatus near the origin without the law of the material being known. The next and more difficult problem is therefore to find the law of flow of the material.

Two methods are possible. They have been named by M. D. Hersey[25] the differentiation method and the integration method. The first consists in the following: After having plotted the consistency curve, let us assume that it is possible to express it in the form of a function

$$V=F(P). \quad (48)$$

Then it has been shown by Weissenberg[26] in the case of the capillary instrument and by Mooney[27] in the case of the rotation instrument, how it is generally possible to derive from (48) through a differentiation process the corresponding Eq. (9) for the material under investigation. The difficulty, however, lies in finding Eq. (48). Weissenberg's method has actually been applied only in the case of simple polynoms as

$$V=a_1P+aP^2 \quad (49)[28]$$

or

$$V=a_1P+aP^3 \quad (49a)$$

and these cases are special cases of the power series Eqs. (43). There exist different methods for determining the coefficients of the power series Eq. (43), and if these are known, the coefficients of the power series Eq. (44) are also known and therefore also the law of flow of the material.

One method consists in extrapolating the V-curve and successive "slope"-curves for $P=0$. Another method which is based on the plotting of the logarithmic homologue of the consistency curve has been used by Weissenberg, Rabino-

[25] M. D. Hersey, J. Rheol. **3**, 23 (1932).

[26] B. Rabinowitsch, Zeits. f. physik. Chemie **A145**, 1 (1929).

[27] M. Mooney, J. Rheol. **2**, 210 (1931).

[28] Such an equation was previously proposed by R. V. Williamson, reference 30.

witsch and Eisenschitz.[29] These methods, which are essentially graphical methods, are found in actual practice to be too uncertain. The uncertainty of extrapolation is well known and the logarithmic method is in this respect not better.

With a limited number of terms it is, of course, possible to calculate the coefficient a to any degree of accuracy by introducing the observed pairs of values V/P and solving the linear equations for the unknown coefficients. For an infinite series the application of this method is only possible if the series converges quickly and can therefore be approximated by a limited number of terms. As will however be shown later, the convergence of the series (43) is usually not very good and as to rheological equations of state of the form (49) or (49a), i.e., with a limited number of terms, there exists a serious objection against them, with which we also will deal later.

13.

The integration method consists in postulating a law of flow of a hypothetical material and checking on the observations whether such a material is a proper model for the material under investigation. If such a law $\dot{e}_i = f(p_i)$ is assumed, it has to be integrated in order to obtain the law $V = F(P)$. If this cannot be effected in closed form, $f(p_i)$ is best expanded into a power series and the integration then leads to a series of the form of Eqs. (43) [or (42)]. This method has been applied successfully in the case of the Newtonian liquid, the Bingham body, etc. The differential equations which form the postulate for these model substances furnish when integrated formulas which quite adequately describe the flow properties as observed with large classes of material bodies. The laws suggested themselves by their simple form: they are *linear* laws. But no linear law is suitable to describe the flow properties of a non-Newtonian liquid. Following this clue of "mathematical simplicity" the problem would therefore be to assume a basic law of as simple a form as possible which conforms to the general shape of the consistency curves of non-Newtonian liquids, to integrate this basic law-differential equation, and compare the resulting consistency curve with actual measurements.

14.

If we examine the consistency curves of non-Newtonian liquids as observed and published until now, we can say that they generally show the following characteristics: The curve starts at the origin and the ordinates (V) increase monotonously with the abscissa (P), i.e., there exists no maximum V. In addition to this the curve generally turns its convex side towards the P-axis. With regard to small V/P values many investigators found that (a) the curve has a finite slope at the origin. With regard to the shape of the curve for large V/P values, Ostwald and his school maintained that (b) there exists an inflection point, after which the curve gradually becomes a straight line which, by extrapolation, passes through the origin (compare Fig. 7). Apart from these empirical findings one can say *a priori* that while the characteristic property of a non-Newtonian liquid is given by the fact that its fluidity increases with increasing shear, this fluidity naturally cannot increase beyond any limit and must finally reach a limiting value. We may denote this value by φ_∞ bearing in mind that it may of course be reached at a large, but *finite* shear.

In the light of the condition (c) it is clear that no polynom with a limited number of terms such as

$$V = a_1 P + a_2 P^2 + \cdots + a_n P^n, \quad n \neq \infty \tag{50}$$

can form the rheological equation of state of a non-Newtonian liquid. For if we divide V by P, we get

$$\varphi' = a_1 + a_2 P + \cdots + a_n P^{n-1}, \tag{51}$$

and unless

$$a_2 = a_3 = \cdots = a_n = 0, \tag{52}$$

which is the case of a Newtonian liquid, φ' cannot have a finite value for $P = \infty$. This is the objection which rules out rheological equations of state of the form of Eqs. (49) and (50), or generally (51). φ' can, however, have a finite value for $P = 0$ if n in Eq. (51) is infinite. The power series so formed, which is identical with the power series Eq. (23) for $\theta = 0$, is the development of a function which has a finite value for $P = \infty$. In special cases, i.e., if the radius of

[29] R. Eisenschnitz, B. Rabinowitsch and K. Weissenberg, Mitt. deutsch. Materialprufüngsanstalten **9**, *Sonderheft* 91 (1929).

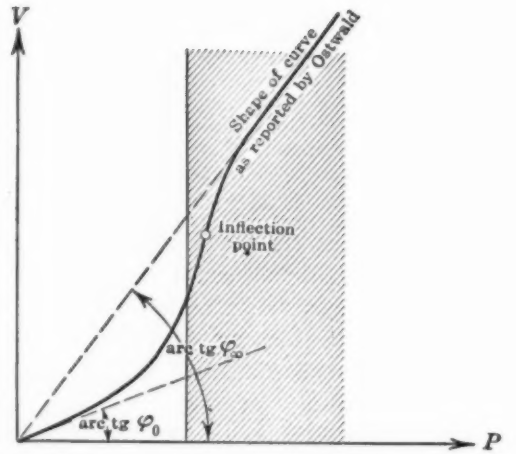

FIG. 7. General shape of the consistency curve of a non-Newtonian liquid.

convergence of the power series is infinite it may even be possible to find the value for φ_∞ from the series by summation without the function f being known, and if the series converges quickly such an expression as Eq. (51) might be a suitable approximation of the series. In order, however, to be justified in taking only two terms, as has been done by Rabinowitsch, or three terms, as has been attempted by Reiner, the series must converge *very* quickly. An examination of the papers mentioned under reference 18 shows that in these cases this was not the case.

A polynom can therefore not form the rheological equation of state of a non-Newtonian liquid. Only in a limited region in the vicinity of the origin can it form an approximation expression of the equation of state. Generally a polynom is therefore not suitable. Looking for another simple mathematical expression, it can be shown that there exists an algebraical function which conforms to all the conditions enumerated at the beginning of the previous section. Such a function has been proposed by Kraemer and Williamson[30] and by Reiner.[18] The objections are however that its coefficients do not allow of a physical interpretation and moreover when integrated the algebraic function becomes a transcendental one and thereby loses its only recommendation, i.e., simplicity.

[30] E. O. Kraemer and R. V. Williamson, J. Rheol. **1**, 76 (1929).

15.

We are therefore forced to abandon the idea of a simple algebraical expression. This, however, robs us of our leading principle in our search for the law of flow of the non-Newtonian liquid. We are accordingly forced to look after some other indication of how to proceed. We may hope to find the right way in which to proceed if we abandon the purely formal treatment and form for ourselves physical concepts through which the consistency curve of a non-Newtonian liquid may be interpreted. Incidentally, we have already become acquainted with two such concepts, i.e., φ_0 the fluidity of material at rest and φ_∞ the maximum fluidity which the material approaches at infinite shear.[31] It should be noted that these quantities are the same whether we consider the apparent or the practical mean or true fluidity. The reason is that all liquids are comparable at the states of rest and infinite shear, i.e., $P=0$ and $P=\infty$ are comparable states.

We can now say that the fluidity of the non-Newtonian liquid increases with increasing shear from φ_0 to φ_∞. The flow condition of the non-Newtonian liquid at a certain shear is therefore characterized by the value of $\varphi_\infty-\varphi$. For a Newtonian liquid this value is equal to zero. The increase from φ to φ_∞ or the consummation of $\varphi_\infty-\varphi$ can be more or less rapid, according to the value of $d\varphi/dp_i$. Between both these quantities there exists the relation

$$C=(\varphi_\infty-\varphi)/d\varphi/dp_i. \tag{53}$$

C is the measure of the hydrodynamic "stability" of the liquid. If $C=0$ (see Fig. 8) the viscosity η_0 of the liquid at rest is at once reduced to η_∞ as soon as the liquid is sheared. The liquid then behaves as a Newtonian liquid with the constant viscosity η_∞ or the constant fluidity φ_∞. If $C=\infty$ the viscosity η_0 of the liquid at rest is not changed at all through shear and in this case also we have a Newtonian liquid with the constant viscosity η_0 or the constant fluidity φ_0. We may therefore call C the "stability coefficient" of the liquid or $1/C$ its "lability coefficient."

A special class of liquids would be the class of all liquids for which C is a constant. If this constant is finite, the liquid is a non-Newtonian liquid.

[31] Care is taken to avoid turbulence.

If C is a constant, Eq. (53) can be integrated. The result is

$$\varphi=\varphi_\infty-(\varphi_\infty-\varphi_0)e^{-p_t/C}. \tag{54}$$

An equation analogous to Eq. (54) can be derived by considering a function relationship of $\eta(\dot{e}_t)$ instead of $\varphi(p_t)$. The result is

$$\eta=\eta_\infty+(\eta_0-\eta_\infty)e^{-\dot{e}_t/C}. \tag{55}$$

For $p_t=0$ and $p_t=\infty$ both equations give the same results $\varphi_\infty=1/\eta_\infty$ and $\varphi_0=1/\eta_0$ because in both these cases $\dot{e}_t$ is also 0 and ∞, respectively. Generally however φ as calculated from (54) is not equal to $1/\eta$ as calculated from (55) and we have two different laws.

It is possible to integrate Eq. (54) in closed form. We get

$$V=\varphi_\infty P-(24C^4/P^3)(\varphi_\infty-\varphi_0)\{1-e^{-P/C}+[1+P/C+(1/2)(P/C)^2+(1/6)(P/C)^3]\} \tag{56}$$

and

$$\varphi^*=\varphi_\infty+(72C^4/P^4)(\varphi_\infty-\varphi_0)\{1-e^{-P/C}[1+P/C+(1/2)(P/C)^2+(1/6)(P/C)^3+(1/18)(P/C)^4]\}. \tag{57}$$

Differential Eq. (55) cannot be integrated in closed form. An attempt at an integration through development into a series was made by Reiner and Riwlin.[32] Eqs. (56) and the analogous equations derived from Eq. (55) give consistency curves which conform to the general shape of the consistency curve of a non-Newtonian liquid as described in Section 14.

16.

Eqs. (56) and (57) enable us to correlate measurements made with different sorts of apparatus as explained in Section 12. Moreover, the coefficients appearing in the rheological equation of state allow of a physical interpretation in terms of macromechanical quantities. This is as far as the phenomenological point of view can lead us. It does, however, not enable us to gain an insight into the processes in the interior of the liquid, which are the cause of its non-Newtonian behavior. In order to gain such an insight, we have to proceed from the phenomenological point of view to the structural, by considering not only macromechanical, but also micromechanical processes.

The first thing then is to note that all non-Newtonian liquids are dispersion systems. No pure homogeneous liquid is known which would not follow Newton's law. The non-Newtonian behavior of a liquid must therefore be due to the changes which are produced in the dispersed phase through the flow. These changes may be either changes of the primary particles themselves or changes in the structures of secondary particles formed by the primary particles. The view that the flow anomalies of the non-Newtonian liquids were due to structural changes was first suggested by E. C. Bingham who called the phenomenon "pseudo-plasticity" and by Wo. Ostwald, who called it "structural viscosity."

A rational solution of the problem has therefore to start with a hydrodynamic theory of dispersed systems.

The methods of classical hydrodynamics allow one, of course, to calculate in principle the dissipation of energy of a flowing liquid in which particles of given shape and size and given mechanical properties are suspended. Actually the mathematical difficulties are however very great and sometimes insurmountable. The viscosity of very dilute systems has been determined by this method in the cases where the suspended particles are (a) rigid spheres, (b) ellipsoids, (c) liquid drops.

The method was first introduced by Einstein who calculated the case (a).

It is based on the following considerations:—If we have a flowing liquid and we imagine part of the liquid to be bounded by a spherical surface, this sphere will be deformed through the flow into an ellipsoid. If the flow is laminar the main axis of the ellipsoid will be inclined to the direction of flow by an angle of 45 degrees and besides the deformation there will also be a rotation of the sphere. If however this sphere is not part of the liquid, but is a rigid body, it will be able to rotate with the liquid but will not be deformed. The presence of the rigid sphere therefore modifies the deformation of the liquid, i.e., it interferes with its "free" flow. By cal-

[32] M. Reiner and R. Riwlin, Koll. Zeits. **43**, 72 (1927); ibid. **44**, 9 (1928).

culating the dissipation of energy of a volume of liquid containing a number of such rigid spheres and comparing it with the dissipation of energy at "free" flow Einstein found that the viscosity $\eta_{soln.}$ of the solution is

$$\eta_{soln.} = \eta_{solv.}(1+C_v/2)/(1-2C_v), \quad (58)$$

where $\eta_{solv.}$ is the viscosity of the solvent and C_v is volume concentration of the solution. This equation is only valid where the particles are so wide apart that they have no influence one upon the other. As furthermore C_v is very small, we can write

$$\eta_{soln.} = \eta_{solv.}(1+2.5C_v+5C_v^2+\cdots) \quad (59)$$

or approximately

$$\eta_{soln.} = \eta_{solv.}(1+2.5C_v). \quad (60)$$

The remarkable feature of Einstein's equation is this, that the size of the suspended particles is irrelevant as long as all are spheres, i.e., all are geometrically similar.

The same method was used by G. B. Jeffery for ellipsoidal particles. Here, however, the mechanism is complicated through the rotation of the particles. The magnitude of interference of the ellipsoidal particle with the free flow depends, of course, on the position of the particle in the liquid, i.e., on the angle between the main axis of the ellipsoid and the direction of flow. This angle, however, is constantly changed through the rotation of the particle in the liquid. If the particle is a sphere all axes of the particle are geometrically equivalent and the rotation is of no influence. Jeffery did not bring the problem to a solution, but he found that in this case the viscosity can also be expressed in the form

$$\eta_{soln.} = \eta_{solv.}(1+aC_v), \quad (61)$$

where a is a constant which depends on the ratio f of the large to the small axis of the ellipsoid. It is of course assumed that all particles are geometrically similar, i.e., in the case of a rotational ellipsoid that f is a constant for every solution.

Eq. (61) can also be written in the following form

$$\eta_{spec.} = \frac{\eta_{soln.}-\eta_{solv.}}{\eta_{solv.}} = \frac{\eta_{soln.}}{\eta_{solv.}} - 1 = n_{rel.} - 1 = aC_v, \quad (62)$$

where $\eta_{spec.}$ is called the "specific" viscosity and $\eta_{rel.}$ is the "relative" viscosity.

R. Eisenschitz calculated a for very long ellipsoids, i.e., when f is very large. He found

$$a_0 = (1.15/\pi)(f/\ln 2f). \quad (63)$$

The calculation was carried out under the assumption that all values of α are equally probable at the beginning of the movement and that the particles become oriented due to the flow of the liquid. If, however, there is a Brownian movement of the particles which completely preserves the isotropic distribution of the main axes of the particles, he found in a later paper

$$a_\infty = f^2/15(\ln 2f - 3/2). \quad (64)$$

We have denoted the coefficient a of Eq. (63) by a_0 because it corresponds to a zero influence of temperature, while a_∞ corresponds to an infinitely great influence of temperature. As can be seen, we have

$$a_\infty > a_0. \quad (65)$$

Generally a will be

$$a_0 < a < a_\infty, \quad (66)$$

depending on the temperature and increasing with increasing temperature.

17.

The non-Newtonian behavior of a dispersed system can be explained from the fact that a suspended particle interferes with the mobility of part of the dispersion medium, if it is assumed that this interference decreases with increased shear. The problem is therefore to explain why and in what manner an increased shear should decrease the interference.

We can distinguish two sorts of interference which we may call (1) interference and (2) immobilization (after a term introduced by Wo. Ostwald).

"Interference" is the mechanism which has been described in the preceding section. "Immobilization" concerns the fact that in "solvated" colloids part of the particle binds part of the dispersion medium so that a larger particle is formed which is suspended as a whole in the dispersion medium. Immobilization is therefore due to solvation.

According to Haller[33] we have to distinguish two sorts of solvation: (a) the "energetic" through "adsorption" and (b) the "steric" through geometrical inclusion.

Lyophilic dispersions will generally show immobilization and interference as well.

Interference can lead in four ways to a non-Newtonian behavior, if the particle is not a rigid sphere.

(a) At rest all values of the above-mentioned angle α are equally probable from which there results a certain viscosity η_0. Through flow α is changed, the particles become more or less oriented. If the orientation is *complete* the viscosity assumes a certain value η_∞. From the investigations of Jeffery and Eisenschitz there follows that $\eta_\infty < \eta_0$. This orientation, however, is counteracted by the rotational diffusion of the Brownian movement. Where the Brownian movement is negligible η_∞ is established as soon as the steady state is reached and the system is therefore Newtonian with the viscosity η_∞. Where the influence of the Brownian movement prevails over the orientation forces η_0 is maintained and in this case also the flow is Newtonian. The first of these cases is characterized by a vanishing stability coefficient C_0, the second by an infinite stability coefficient. (See Fig. 8.) Generally there will be at every temperature and every shear a dynamical equilibrium between the forces of diffusion and orientation, with a corresponding η, where $\eta_0 > \eta > \eta_\infty$. This is according to Staudinger the mechanism of non-Newtonian behavior. As has, however, been shown in the preceding section, the relative viscosity must in this case be dependent on the temperature. An increase of temperature brings with it increasing Brownian movement and therefore a shifting of η towards η_0. $\eta_{rel.}$ therefore increases with temperature.

(b) The interruption of the deformation of the liquid produced by reaction in the particle tensional stresses. Through these stresses the particle is deformed. The deformation may be considerable. For example, it has been assumed in order to explain the elasticity of rubber that the rubber molecule is formed like a spring. In this case the molecule will be extended elastically. The tension and extension is at its highest when the axis of the spring has the direction of the principal stress. This direction is inclined by an angle of 45 degrees towards the direction of flow. As has, however, been explained before, the particle is not only deformed, but also rotates. Through rotation the spring is unloaded and recovers. This results in an oscillation of the particle, which is transmitted to the liquid and by this therefore the amount of dissipated energy is increased. If such a mechanism exists, the result must therefore be an *increase* of the relative viscosity, the same as through turbulence.

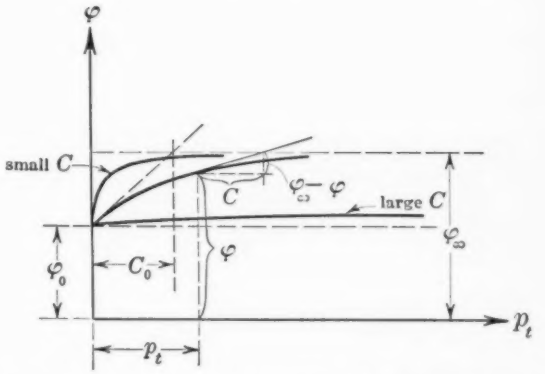

FIG. 8. Fluidity as affected by the stability coefficient, C.

(c) If the particles are threads without rigidity, as has been assumed by Haller the result is entirely different. The tension produces a straightening out of the thread. This decreases the viscosity because the particle is giving way. Rotation of the particle tends to restore a random distribution. It is difficult to judge the influence of change of temperature; $\eta_{rel.}$ may be independent of temperature.

(d) If the tension is very great, or the breaking strength of the particle very small, the particle breaks as soon as its axis coincides with the direction of main stress. The particle can also be broken through bending. Staudinger pictures his rod molecules as of very small strength and easily broken. Shortening of the particle decreases f in Eqs. (63) and (64) and therefore decreases η. Whenever the fragments touch each other in a suitable position, the particle may be reformed. The probability for this is, however, small. The consistency curve must in this case therefore show a hysteresis loop.

[33] W. Haller, Koll. Zeits. **57**, 197 (1931).

TABLE II. *Types of non-Newtonian behavior.*

	(A) Variation of $\eta_{rel.}$ with temperature	(B) Reversibility—absence of a hysteresis loop	(C) Existence of a lower limit of non-Newtonian behavior
1. Disturbance			
a. Competition between orientation and Brownian movement	increases	yes	no
b. Elastic deformation	?	yes	no
c. Thread deformation	?	yes	no
d. Adsorption	nil	no	yes
2. Immobilization			
a. Adsorption	decreases	yes	yes
b. Steric immobilization (structural viscosity)			
α Macromolecule	?	no	yes
β Micelle	?	no	yes
γ Ordered group	?	no	yes
δ Unordered aggregate	nil or decreases	yes	yes

(2a) In the case of immobilization through adsorption a non-Newtonian behavior can be explained by a shearing off of the adsorption layer. Such a mechanism has been suggested by Hatschek and mathematically formulated by Reiner and Riwlin.[32] In this case there must be an influence of change of temperature. As many have pointed out adsorption is an exothermal process and should decrease with increasing temperature. In this case $\eta_{rel.}$ therefore decreases, with increased temperature.

(2b) The steric immobilization has been discussed at great length by Kraemer and Williamson.[3] They imagine the particle to be "an ultramicroscopic body which is generally permeated in jel-like fashion with the liquid medium. The union of the structural elements forming the particle may involve any or every type of bond which can operate between atoms or molecules." The particle may be either (α) a giant molecule, immobilizing solvent between the branches and in its ring, (β) a micelle (crystallite), (γ) a group of micelles with a regular arrangement, or (δ) an aggregate or unordered assemblage of smaller particles.

A non-Newtonian behavior can result in two ways: (I) through deformation, (II) through destruction. With regard to (I) it should be noted that the particle can be much deformed. It will therefore partially participate in the deformation of the liquid. Such a deformation of the particle will squeeze out of it solvent as from a sponge, i.e., part of the dispersion medium is being mobilized. With regard to (II) it should be noted that the deformation is accompanied by stresses. These stresses the particle can only resist to a certain limit. If this limit is exceeded the particle breaks and this again makes free part of the immobilized liquid. If the fragments of the particles come to touch each other in the course of flow, the particles may be reformed. "For a particular rate of shear, a dynamic equilibrium would be established between the the rate of disaggregation and the rate of reaggregation." It should, however, be noted, that the probability of reaggregation is generally not the same as that of disaggregation. Both are equal only in the case of group (2b, 8), i.e., in the case of unordered aggregates. Only in this case every meeting of the fragments in any position can result in a reaggregation. In the case of molecules, micelles and ordered aggregates a binding of the fragments can only take place if the fragments are in a *certain* position. Not every position is therefore equally favorable. If the consistency-measurements are made in both ways, i.e., the shear is increased from zero to a maximum and then decreased to zero again, there will result not a single curve, but two such curves forming a hysteresis loop.

It is not possible to say *a priori* what the influence of a change of temperature should be in the case of steric immobilization. There is the possibility that $\eta_{rel.}$ may not change at all with temperature. However, it is mostly assumed that in the case of an unordered aggregate the binding forces are so small that the aggregate will

partially be destroyed by an increase of temperature.

Table II gives a summary of all these mechanisms and their properties.

18.

The considerations of Section 17 lead to the conclusion that there may exist different types of non-Newtonian liquids. We have three criteria which may enable us to decide whether a given non-Newtonian liquid belongs to one type or another. They are (A) The influence of a variation of the temperature on $\eta_{rel.}$; (B) the reversibility or irreversibility of a variation of shear; (C) the existence of a lower limit of non-Newtonian behavior.

With regard to (A) it is obvious that $\eta_{rel.}$ cannot show a dependence on the temperature as long as the phenomenon of a non-Newtonian behavior is entirely of geometric-mechanical character. In this case the vibration of the viscosity of the solution with temperature is solely due to the variation of the viscosity of the *solvent*. (1d) represents such a mechanism, as it consists in a breaking, i.e., a shortening of the particle. Here the non-Newtonian change of viscosity is entirely due to a change of the geometrical shape of the particle. On the other hand, we can say that there must be a dependence on temperature in the case (a). A dependence must also exist in the case (2a). Nothing can be said *a priori* with regard to the other mechanisms.

With regard to (B) we have already said that an *instantaneous* change of viscosity with changing shear, i.e., without any lag is only possible if all positions of the particles are equally favorable for a reaggregation. This is not the case if the particles are molecules or micelles.

With regard to (C) it should be noted that wherever the non-Newtonian behavior is due to a partial destruction of the structure (2b), (b), (c), (d) or to a shortening of the primary particle (1d, 2a) the non-Newtonian behavior must show a lower limit. The forces which form either the primary particles or the secondary structures can of course only be overcome when the stresses produced through the flow reach and exceed a certain value. Up to this value the behavior of the system is normal, i.e., Newtonian.

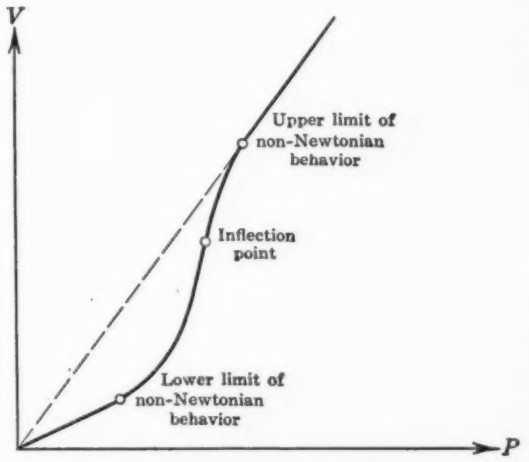

FIG. 9. Generalized Ostwald curve.

Such a limit cannot exist in the cases (1a, b, c) where the smallest stress must be of influence.

It should be furthermore noted that all mechanisms require that when η_∞ is reached, the liquid behaves Newtonian. This value of η_∞ may, of course, be reached either at a finite shear or only at infinite shear. In both cases the consistency curve must have the shape predicted by Wo. Ostwald (Fig. 9).

Experiments made up to now with non-Newtonian liquids have not provided enough information to decide which type of non-Newtonian behavior the liquid represents. It is necessary to make the observations with instruments of varying dimensions in order to decide whether there is a wall-effect or not. It is furthermore necessary to use both the rotation type and the capillary tube type of instrument in order to cover a wide enough range of shear. Furthermore the temperature also must be changed.

Such an investigation has recently been made with rubber-toluene solutions and it was found that these solutions belong to type (2b, δ).

I want also here to thank Professor E. C. Bingham for the interest he has taken in this investigation and the valuable suggestions which he made in the numerous discussions. My thanks are also due to those benefactors and the Chemical Foundation whose financial assistance made possible the research of which this paper is an outcome.

Viscometric Studies of Rubber Solutions

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Support for the assumption that rubber particles in rubber-toluene solutions are solvated unordered aggregates is derived from a quantitative study of viscometric measurements, which shows that the forces acting between the primary particles (structural elements) must be very small.

A FORMER communication[1] reported viscometric observations on rubber-toluene solutions in different capillary and rotation-viscometers. The consistency curve of solutions from 0.08 to 1.77 percent concentration starts at the origin as a straight line inclined at a definite angle, until it reaches a certain point a (see Fig. 1). From there it becomes convex toward the stress-axis. This convex part extends to an inflection point b where the curve becomes concave up to a point c; where it again becomes a straight line which by extrapolation passes through the origin. The solutions therefore behave as Newtonian liquids between points o and a, and c and ∞. Between point a and c they are non-Newtonian liquids.

It was furthermore shown that the "relative" consistency curve, i.e., a curve in which the shearing stress is reduced or the rate of shear increased in proportion to the viscosity of the solvent, is independent of the temperature at which the viscosity measurement is made. From this latter property the conclusion was drawn that the phenomenon of non-Newtonian behavior is a purely mechanical one. It cannot be due, as has been suggested by Staudinger,[2] to a competition between orientation due to laminar flow and rotational diffusion due to Brownian movement, because the magnitude of the latter depends on the temperature.

The independence of the temperature also rules out the assumption of an adsorption layer of variable thickness, proposed by others, because the thickness of such an adsorption-layer can hardly be independent of the temperature. It was accordingly concluded that the non-Newtonian behavior must be due to the rubber-particles in solution being, "gel-fragments," or secondary particles "permeated in gel-like fashion with the liquid medium" as suggested by Kraemer and Williamson.[3] This model explains the existence of point a. It is defined by the strength of the bond between the primary particles or structural elements. Until the stresses produced in the secondary particles by the flow-deformation reach this breaking strength, the solution must naturally behave as a Newtonian liquid. When the shear is increased beyond this point, the secondary particles are broken up to form primary particles, releasing at the same time liquid medium. This increases the fluidity of the solution and causes the curve to become convex. The fragments formed through the process just described, reaggregate when coming in contact in the course of flow and a dynamic equilibrium may establish itself between the disaggregation and reaggregation.

According to the bond, which operates between the primary particles, the secondary particles can be either macromolecules, micelles, ordered or unordered groups. The first three types however have the property in common that the fragments will not reunite at every chance encounter, but only when they meet in certain orientations to each other. As a result, a time-lag should be observed if a closed consistency curve were described, i.e., the consistency-curve should show a hysteresis loop. This was not found to be the case by our observations. Regardless of whether the rate of shear was being increased or decreased, the observational points fall upon a single smooth curve. This excludes the possibility of ordered aggregates and therefore leaves as the

[1] M. Reiner and R. Schoenfeld-Reiner, Koll. Zeits. **65**, 44 (1933).

[2] H. Staudinger, *Die hochmolekulare org. Verbindungen*, p. 189, Berlin, 1932.

[3] E. O. Kraemer and R. V. Williamson, J. Rheology **1**, 76 (1929).

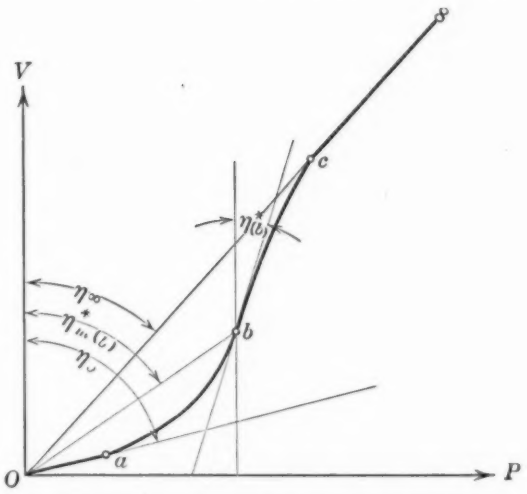

FIG. 1. General shape of the consistency curve.

only possibility of unordered aggregates of primary particles, held together by cohesive forces, the primary particles themselves being either macromolecules, micelles, or ordered groups. These preliminary conclusions drawn from the observations were purely qualitative. In the present paper we will treat some of our experimental data quantitatively.

The quantitative relation which is most commonly looked for in viscometric observations with solutions of different concentrations is one between viscosity and concentration. When, however, a non-Newtonian liquid flows through a tube (or any other viscometer), there prevails in each telescopic layer a different rate of shear and therefore a different viscosity. It is therefore generally impossible to speak of the viscosity of the liquid at a certain efflux, corresponding to a certain point on the consistency curve. While rubber toluene solutions are generally non-Newtonian liquids, it was found that there exist two regions in which the solutions behave as Newtonian liquids. In these regions definite constant viscosities therefore exist, which we may denote by η_0 and η_∞.

The viscosity, η_0, at rest and up to the point a may be called the "zero-viscosity." The relative zero-viscosities of different solutions were determined from our observations and are shown in Table I. Table I also shows the "specific" viscosity, which is defined by

$$\text{specific } \eta = \text{relative } \eta - 1 \tag{1}$$

TABLE I. *Relative and specific zero-viscosities and fluidities.*

No. of solution	II	19	7	6	4	3	2.1	2
Concentration								
$10^2 c_v$	1.71	1.48	0.98	0.97	0.23	0.17	0.11	0.08
rel η_0	185	108	36.2	27.3	2.55	2.15	1.76	1.60
rel φ_0	.00541	.00943	.0276	.0366	.3922	.4651	.5681	.625
spec η_0	184	107	35.2	26.3	1.55	1.15	0.76	0.60
a_0	10800	7240	3600	2700	670	680	690	750

and **a**, the specific viscosity per unit of concentration, i.e.,

$$\mathbf{a} = \text{specific } \eta / c_v, \tag{2}$$

where c_v is the volume-concentration of the solution.

In Fig. 2 rel η_0 and $\mathbf{a}_0$ have been plotted as functions of c_v. As can be seen from this figure, rel η_0 is linear and $\mathbf{a}_0$ constant up to $c_v = 0.3$ percent, corresponding to a value of spec $\eta_0 = 2$. This is remarkably high, as it is usually assumed that with solutions of high molecular substances the simple linear relationship has its limit with spec $\eta_0 = 0.3$.[4] The constant value of $\mathbf{a}_0$ is 700. This can be interpreted as follows: (a) For very dilute suspensions of spherical particles Einstein derived the formula

$$\text{specific } \eta = 2.5 C_v, \tag{3}$$

where C_v is the concentration of the suspended particles. If the suspended particles are solvated, i.e., if they immobilize part of the dispersion-medium, we have

$$C_v = b c_v, \tag{4}$$

where $b > 1$. b has been called the specific hydrodynamic volume of the material.

Introducing the value for C_v from (4) into (3) we get

$$\text{specific } \eta = 2.5 b c_v \tag{5}$$

and by considering (2)

$$\mathbf{a} = 2.5 b \quad \text{or} \quad b = \mathbf{a}/2.5. \tag{6}$$

In our case we would have

$$b_0 = 700/2.5 = 280, \tag{7}$$

i.e., if the dispersed solvated rubber particles were of a spherical shape, the volume of the immobilized liquid would be 279 times the

[4] E. Guth and H. Mark, *Ergebnisse*, p. 118, Berlin, 1933.

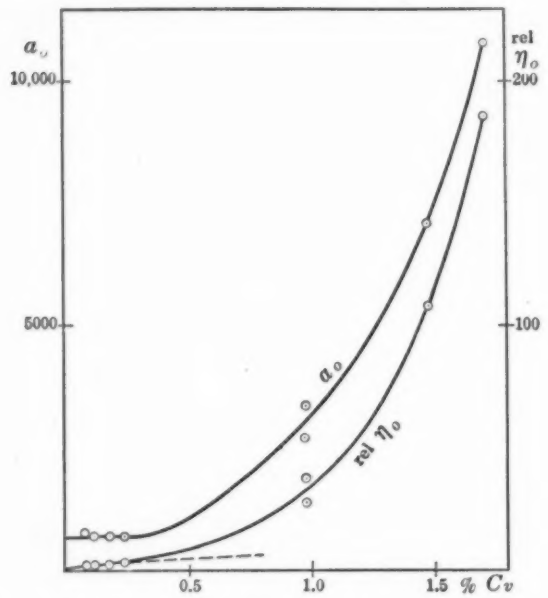

FIG. 2. Relative zero viscosities for different concentrations.

volume of the dispersed rubber and the particle concentration of our solutions, 2, 2.1, 3, and 4 would be 22, 31, 48, and 65 percent, respectively. This however is not possible. Einstein's equation is valid for very dilute solutions only, and it is well known that the viscosity increases linearly with concentration at small concentrations only. As has been said before the increase of viscosity is linear and quite small up to $c_v = 0.30$ percent.

If the real concentration corresponding to $c_v = 0.30$ percent was $280 \times 0.3 = 84$ percent, this would be out of question. The actual ratio of volume of immobilized liquid to volume of rubber must therefore be much smaller than 279. (b) Einstein's[5] formula (3) can be generalized to

$$\text{specific } \eta = A C_v \tag{8}$$

for particles of general (non-spherical) shape, where A is a different constant for every different shape of the particle, being equal to 2.5 in the case of a sphere. Eisenschitz[6] could show that under certain assumptions

$$A = \frac{1.15}{\pi} \cdot \frac{l}{d} \cdot \frac{1}{\ln 2l/d} \tag{9}$$

in the case of very long rotational ellipsoids of length l and thickness d.

If c_v were the true volume-concentration of the dispersed phase, i.e., if the dispersed rubber was not solvated, and if we had reasons to assume that the particles are long rotational ellipsoids, we could calculate from Eq. (9) that

$$\frac{l}{d} \cdot \frac{1}{\ln l/d} = \frac{700\pi}{1.15} = 1910 \tag{10}$$

or

$$l/d = 20{,}000, \tag{11}$$

which means that the particles were of a length of 20,000 times their thickness. We know, however, that this cannot be the case, as the particles are solvated. We have therefore to picture the particles as solvated to less than 279 times and elongated to less than 20,000 diameters.

Table II shows possible combinations of solvation and elongation. Under C_v the particle concentration up to which the viscosity-concentration relation is linear, is shown. Beyond this, we cannot at this stage, draw any conclusions about the shape of the particle and the quantity of liquid imbibed.

TABLE II. *Possible combinations of solvation and elongation for $a = 700$.*

l	280	100	10	1
l/d	1	20	1500	20,000
C_v	84%	30%	3%	0.3%

This is how far the information provided by the first straight part of the consistency-curve up to point a carries us. Next the establishment of a relation between the position of the point a and the concentration may be undertaken.

We said that the existence of a point a (Fig. 1) must be interpreted as indicating the starting of a mechanical disaggregation of the suspended rubber-particles, through the breaking off of primary particles. This breaking off is caused by the stresses, produced in the particle through the flow of the solvent, when these stresses exceed the breaking strength β of the particles. We know from our data (see Fig. 3) the shearing stress ($\bar{P}$) and relative rate of shear ($\bar{V}_{rel}$) at which a is reached in the case of some of the solutions and it should be possible to find a

[5] A. Einstein, Ann. d. Physik **19**, 289 (1906); **34**, 591 (1911).
[6] R. Eisenschitz, Zeits. f. physik. Chemie **A158**, 78 (1931).

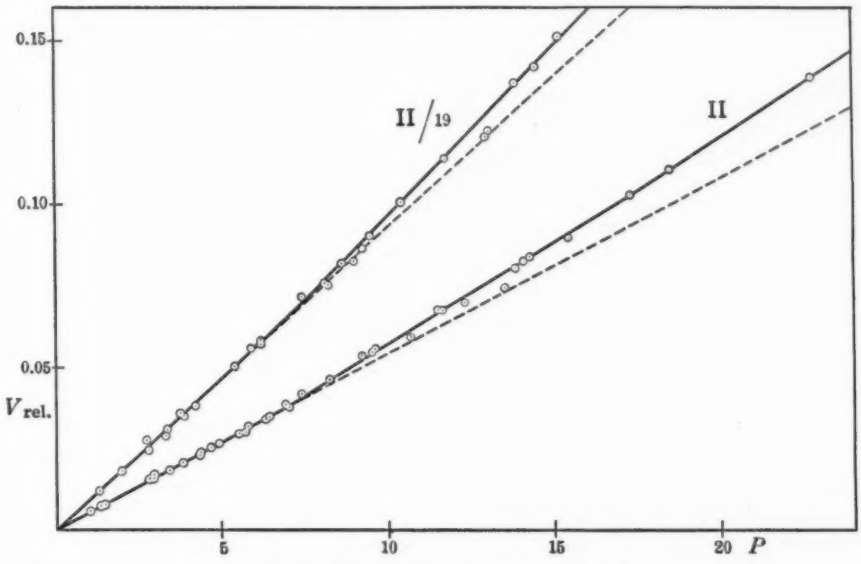

FIG. 3. Consistency curves at low rates of shear.

relation between these magnitudes and the breaking strength of the particle. Such a relation can be theoretically derived on the basis of Einstein's calculation of the viscosity of a solution as shown in the Appendix. The result is as follows: Let $\bar{V}_{rel}$ be the relative shearing velocity of laminar flow, then a tensional stress S_t is developed in the particle, the magnitude of which is

$$S_t = n\bar{V}_{rel}, \tag{12}$$

where n is a numerical factor, which in the case of spherical particles is equal to 5 and for "elongated" particles is greater than 5. The stress acts in a direction inclined under 45° against the direction of flow. It is independent of the concentration, the size of the particle and is the same in every point of the particle.

The particle begins to disaggregate as soon as S_t reaches the breaking strength β. Disaggregation will therefore start at the limiting relative shearing-velocity

$$\bar{V}_{rel} = p/n. \tag{13}$$

The limiting relative shearing-velocity is therefore independent of the concentration.

On the other hand $\bar{P}$, the limiting shearing stress, is

$$\bar{P} = \eta_{rel} \cdot \bar{V}_{rel} = (p/n)\eta_{rel} \tag{14}$$

and as η_{rel} depends on c_v, $\bar{P}$ depends in the same way on c_v. This seems not to be confirmed by Fig. 3. Here it looks as if on the contrary $\bar{P}$ was independent of c_v and $\bar{V}_{rel}$ was decreasing accordingly. It should, however, be born in mind that the consistency-curves (Fig. 3) refer to the solutions II and 19 with the high concentration of 1.71 and 1.48 percent. For such concentrations our Eqs. (13) and (14) are not valid. Unfortunately, in the more dilute solutions the point a could not be reached at the maximum shear produced in the Couette-apparatus.

Solutions II/2 and II/18, both with the same concentration of 0.08 percent were however measured in the Couette and Bingham-viscometer and it was therefore thought possible to find $\bar{P}$ and $\bar{V}_{rel}$ by a graphical comparison of the measurements in both instruments. Such a graphical comparison is made difficult by the fact that the shear produced in the capillary-instrument is so much larger than the shear produced in the rotation-instrument that a graph, as usually plotted becomes unwieldy. This difficulty is partly overcome by plotting on a logarithmic scale. In the same way the measurements of solution III/14 and 13 and II/15 in the Bingham-instrument were compared with the hypothetical between the measurements in a Couette-instrument derived by intrapolation

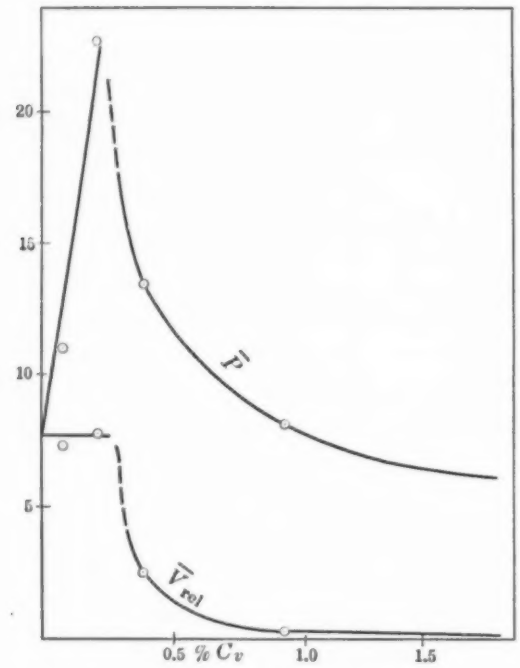

FIG. 4. Limiting rates of shear and shearing stresses.

between the measurements made with solutions II/17, II/6, II/4 and 3. The results are shown in Table III and in Fig. 4. Fig. 4 confirms our Eqs.

TABLE III.*

No. of solution	II	19	14	13	15	18
$10^2\, c_v$	1.71	1.48	0.39	0.38	0.21	0.08
$\bar{V}_{rel}$	0.034	0.058	2.55		7.79	7.35
$\bar{P}$	6.30	6.30	13.5		22.7	11.0

* Because of the method used in the determination of $\bar{V}_{rel}$ and $\bar{P}$, the values given for solutions 14, 13, 15 and 18 are very approximate.

(13) and (14) for very dilute solutions. At concentrations over 0.25 percent, however, both $\bar{V}_{rel}$ and $\bar{P}$ fall rapidly, the latter tending towards a constant. The concentration of 0.25 percent is also approximately the concentration at which $\bar{V}_{rel}$ ceases to increase linearly (see Fig. 2), i.e., this is the concentration at which the suspended particles influence one another in their hydrodynamic behavior. It may be expected that such an influence should bring with it a rapid decrease of $\bar{V}_{rel}$ and $\bar{P}$.

The results of the proceeding section confirm our interpretation of the point a of the consistency curve and therefore also of our model for the suspended particle and the mechanism of the non-Newtonian behavior. For very dilute solutions $\bar{V}_{rel}$ tends to become constant with the value 7.70. According to equation (13) we have

$$\beta = 7.70n \text{ dynes/cm}^2.$$

We do, however, not know n, as we do not know the shape of the particle and are therefore not in a position to calculate β, the breaking strength of the suspended particles. This breaking strength is not identical with the cohesion of the rubber because in the solution the cohesion forces in the rubber are counteracted by the adhesion between rubber and solvent. Moreover the inclusion of the solvent reduces the massive section of the particle. It is not possible to calculate this reduction, as we do not know the volume of the solvent, which is immobilized by the rubber particles. We can nevertheless say that the bond between the primary particles, as measured by β, is very small. If we take $n = 5$ we get $\beta = 38$ dynes/cm^2 and this is about 10^{-7} the tensional strength of rubber. It can hardly be assumed that n should be so large as to make up this difference. We must therefore conclude that the forces which combine the primary particles to the secondary particles are very small.

The present quantitative analysis of the results of viscometric measurements with rubber-toluene solution has furnished new support for

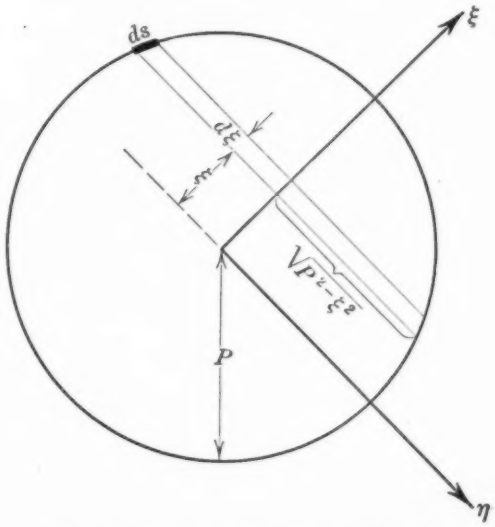

FIG. 5. Stresses in a spherical particle.

the model of solvated unordered aggregates, suggested for the suspended rubber particles. It was however not possible to calculate the amount of immobilized solvent and therefore also not the size of the suspended particles. It is thought that this can only be accomplished by combining some other measurements with the viscometric measurements as, e.g., diffusion measurements.

I am glad to express my gratitude to Dr. E. C. Bingham for the interest taken in this research and to those benefactors who have made it possible.

Appendix

To calculate the stresses produced in the particle through its interference with the free flow of the liquid, we start from the following equations of Einstein's paper (page 295)

$$X_\xi = p - 2k\frac{\partial u}{\partial \xi}; \qquad Y_\zeta = Z_\eta = -k\left(\frac{\partial v}{\partial \zeta} + \frac{\partial w}{\partial \eta}\right) \qquad \begin{pmatrix} X, & Y, & Z \\ \xi, & \eta, & \zeta \\ u, & v, & w \end{pmatrix}^*, \quad (1)$$

where u, v and w are according to Eq. E(6)**

$$u = A\xi - \frac{5}{2}\frac{P^3}{\rho^5}\xi(A\xi^2 + B\eta^2 + C\zeta^2) + \frac{5}{2}\frac{P^5}{\rho^7}(A\xi^2 + B\eta^2 + C\zeta^2) - \frac{P^5}{\rho^5}A\xi \qquad \begin{pmatrix} A, & B, & C \\ \xi, & \eta, & \zeta \\ u, & v, & w \end{pmatrix} \quad (2)$$

and

$$\rho = (\xi^2 + y^2 + \zeta^2)^{\frac{1}{2}}. \quad (3)$$

From (2) there follows

$$\frac{\partial u}{\partial \xi} = A - \frac{5}{2}\frac{P^3}{\rho^5}\xi \cdot 2A\xi - \frac{5}{3}\frac{P^3}{\rho^5}(A\xi^2 + B\eta^2 + C\zeta^2) + \frac{5}{2}P^3\xi(A\xi^2 + B\eta^2 + C\zeta^2)\frac{5}{\rho^6}\frac{\partial \rho}{\partial \xi} + \frac{5}{2}\frac{P^5}{\rho^7}\xi \cdot 2A\xi$$

$$+ \frac{5}{2}\frac{P^5}{\rho^7}(A\xi^2 + B\eta^2 + C\zeta^2) - \frac{5}{2}P^5\xi(A\xi^2 + B\eta^2 + C\zeta^2)\frac{7}{\rho^8}\frac{\partial \rho}{\partial \xi} - \frac{P^5}{\rho^5}A + P^5A\xi\frac{5}{\rho^6}\frac{\partial \rho}{\partial \xi}. \quad (4)$$

From (3) there follows

$$\partial\rho/\partial\xi = 2\xi/2(\xi^2 + \eta^2 + \zeta^2)^{\frac{1}{2}} = \xi/\rho. \quad (5)$$

Introducing $\partial\rho/\partial\xi$ from (5) and putting $\rho = P$, Eq. (4) becomes

$$\left.\frac{\partial u}{\partial \xi}\right|_{\rho=P} = \frac{5\xi^2}{P^2}\left[A - \frac{1}{P^2}(A\xi^2 + B\eta^2 + C\zeta^2)\right] \qquad \begin{pmatrix} u, & v, & w \\ \xi, & \eta, & \zeta \\ A, & B, & C \end{pmatrix}. \quad (6)$$

Similarly we get

$$\left.\frac{\partial u}{\partial \eta}\right|_{\rho=P} = \frac{5\eta\xi}{P^2}\left[A - \frac{1}{P^2}(A\xi^2 + B\eta^2 + C\zeta^2)\right] \qquad \begin{pmatrix} u, & v, & w \\ \xi, & \eta, & \zeta \\ A, & B, & C \end{pmatrix}. \quad (7)$$

Furthermore we have

$$1/\rho = 1/(\xi^2 + \eta^2 + \zeta^2)^{\frac{1}{2}} \quad (8)$$

and therefore

$$\frac{\partial(1/\rho)}{\partial \xi} = -\frac{\xi}{\rho^3}; \qquad \frac{\partial^2(1/\rho)}{\partial \xi^2} = \frac{2\xi^2\eta^2 - \zeta^2}{\rho^5} = \frac{3\xi^2 - \rho^2}{\rho^5} \qquad (\xi, \eta, \zeta). \quad (9)$$

If we introduce the expressions for $\partial^2(1/\rho)/\partial\xi^2$, $\partial^2(1/\rho)/\partial\eta^2$, and $\partial^2(1/\rho)/\partial\zeta^2$ into the first of Eqs. E(5) we get

* $\begin{pmatrix} X, & Y, & Z \\ \xi, & \eta, & \zeta \\ u, & v, & w \end{pmatrix}$ means that X, Y, Z, ξ, η, ζ, u, v, w should be permuted cyclically in order to obtain two more analogous equations.

** E (6) means Eq. (6) in Einstein's paper.

$$p=-\frac{5}{3}kP^3\left\{A\frac{3\xi^2-\rho^2}{\rho^5}+B\frac{3\eta^2-\rho^2}{\rho^5}+C\frac{3\zeta^2-\rho^2}{\rho^5}\right\} \tag{10}$$

and considering Eq. E(2) and putting $\rho=P$ this gives

$$p\Big|_{\rho=P}=-\frac{5k}{P^2}(A\xi^2+B\eta^2+C\zeta^2). \tag{11}$$

We now introduce the values from (6), (7) and (11) into Eqs. (1) and get the following expressions for the components of the stresses acting on the surface of a small spherical particle

$$\left.\begin{aligned} X_\xi&=-\frac{5k}{P^2}\left[\left(1-2\frac{\xi^2}{P^2}\right)(A\xi^2+B\eta^2+C\zeta^2)+2A\xi^2\right]\\ Y_\xi=Z_\eta&=+\frac{5\eta\zeta k}{P^2}\left[\frac{2}{P^2}(A\xi^2+B\eta^2+C\zeta^2)+A\right]\end{aligned}\right\}\qquad \begin{pmatrix}X,\ Y,\ Z\\ \xi,\ \eta,\ \zeta\\ A,\ B,\ C\end{pmatrix}. \tag{12}$$

In Eqs. (12) we have gained expressions for the six components of the stress tensor in every point of the surface of the particle with the coordinates ξ, η, ζ, where

$$\xi^2+\eta^2+\zeta^2=P^2. \tag{13}$$

We now want to know the three components of the forces per unit area of the surface of the particle, parallel to the axes ξ, η and ζ and exerted by the liquid upon the particle.

They can be calculated from the Eqs. (12) by means of Einstein's equation page 295

$$X_n=-(X_\xi\xi/P+X_\eta\eta/P+X_\zeta\zeta/P)\qquad \begin{pmatrix}X,\ Y,\ Z\\ \xi,\ \eta,\ \zeta\end{pmatrix}. \tag{14}$$

We get

$$-X_n=\frac{5k}{P^3}\left\{(A\xi^2+B\eta^2+C\zeta^2)\left[-\xi+2\frac{\xi}{P^2}(\xi^2+\eta^2+\zeta^2)\right]+\xi(-2A\xi^2+B\zeta^2+C\eta^2)\right\}$$

$$=\frac{5k\xi}{P^3}[-A\xi^2+B(\eta^2+\zeta^2)+C(\eta^2+\zeta^2)]=\frac{5k\xi}{P^3}[-AP^2+(\eta^2+\zeta^2)(A+B+C)] \tag{15}$$

and if we consider Eq. E(2) this gives

$$X_n=5kA\xi/P,\qquad Y_n=5kB_\eta/P,\qquad Z_n=5kC\zeta/P. \tag{16}$$

For every value of ξ between ξ and $\xi=P$ we have a calote on which the hydrodynamic force

$$X=\int_\xi^P 2(P^2-\xi^2)^{\frac{1}{2}}\pi X_n ds \tag{17}$$

acts (see Fig. 5). It can easily be seen that

$$ds=[P/(P^2-\xi^2)^{\frac{1}{2}}]d\xi. \tag{18}$$

Introducing ds from (18) into (17) we get

$$X=2P\pi\int_\xi^P X_n d\xi=2P\pi\frac{5kA}{P}\int_\xi^P \xi d\xi=5\pi kA(P^2-\xi^2). \tag{19}$$

This force produces internal stresses in the particle which in a section normal to ξ axis and at the distance ξ are equal to

$$p_\xi \equiv X/(P^2-\xi^2)\pi = 5kA \qquad \begin{pmatrix} \xi, & \eta, & \zeta \\ A, & B, & C \end{pmatrix}. \quad (20)$$

This result is quite remarkable. Eq. (20) says that the stress is independent of P and ξ, i.e., the reaction of the liquid against the interference of its free flow by a spherical particle, produces in this particle internal stresses which are independent of the size of the particle and are the same for every parallel section through the particle.

We have derived the stresses produced in the spherical particle under the assumption that there is only one particle suspended in the liquid. We now have to proceed to the case when there are many particles suspended in the liquid, which case is dealt with in §2 of Einstein's paper. In equations (20) A, B, C are the main extension-velocities of the liquid, if there was no spherical particle suspended. These have to be replaced by the main extension-velocities A^*, B^* and C^*, of the "solution." We get accordingly

$$p_\xi^* = 5kA^* \qquad \begin{pmatrix} \xi, & \eta, & \zeta \\ A^*, & B^*, & C^* \end{pmatrix}, \quad (21)$$

where the symbol* refers to the solution. According to our definition of V_{rel}, we have

$$A_{\text{rel}} = kA^* \qquad (A, B, C), \quad (22)$$

and therefore

$$p_\xi^* = 5A_{\text{rel}} \qquad \begin{pmatrix} \xi, & \eta, & \zeta \\ A, & B, & C \end{pmatrix}. \quad (23)$$

From considerations of mechanical similarity we may conclude that for particles of *any* shape Eq. (23) can be generalized to

$$S_t = nV_{\text{rel}}, \quad (24)$$

where S_t is the tensional stress produced in the particle, V_{rel} is the relative shearing-velocity and n is a numerical factor which in the case of a sphere is equal to 5 and for "elongated" shapes must be greater than 5.

The Conicylindrical Viscometer

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(Received June 22, 1934)

INTRODUCTION

WHEN making rheological measurements on non-Newtonian liquids, especially those that are thixotropic, it is highly desirable to use an instrument in which the liquid is subjected to continuous and uniform or essentially uniform stresses. Otherwise the data cannot be interpreted without ambiguity or questionable assumptions. The rotating cylinder viscometer in its various forms is the only viscometer so far developed that meets this requirement; but it is usually made difficult to clean and is complicated mechanically by guard rings placed at the ends of the inner cylinder to eliminate end effects. The upper guard ring can easily be dispensed with if the liquid level in the viscometer is kept below the top of the cylinders. The lower guard ring, also, has recently been eliminated by an ingenious design, used by Mercier,[1] in which an air pocket in a concavity in the lower end of the inner cylinder practically eliminates shearing stresses over the bottom surface.

The essential feature of a new design described in the present article consists in such a formation of the lower ends of the two cylinders that the ratio of the clearance between them at any point to the radial distance of the point from the axis is constant and is equal, at least approximately, to the ratio of the clearance to the radial distance at the sides of the cylinders. The rate of shear in the liquid at the bottom will therefore be essentially the same as at the side. The outstanding feature of the rotating cylinder viscometer is thereby retained, while the guard rings are eliminated without the introduction of an air pocket at the bottom.

In the form of the instrument described below, called the conicylindrical viscometer, the bottom surfaces of the two cylinders are cones of slightly different angle. The hydrodynamical analysis of the conical region will first be developed, after which the instrument, as built, will be described in detail.

[1] P. Mercier, J. Rheology **3**, 391 (1932).

HYDRODYNAMIC ANALYSIS

The complete notation is given in the table at the end of the paper. Referring to Fig. 1, let a and b be the radii of the inner and outer cylinders, respectively, and α and β the corresponding angles of the conical bottoms. We need to analyze the hydrodynamics of the region between the conical surfaces only, the solution for the cylindrical surfaces being known. Let r, θ, Φ be a system of spherical coordinates as indicated.

Suppose that the lower cone is rotating in the positive direction with angular velocity ω, that the upper cone is stationary, and that the space between them is filled with a liquid of fluidity φ. The fluidity is not assumed to be independent of shearing stress.

It can be shown from the complete system of stress equations and boundary conditions that, inertia being neglected, the liquid at any particular point is rotating about the axis of the system with a velocity, v, which is a function of the coordinates r and θ; that the other two velocity components are zero; and that the only shearing stress different from zero is the one acting in the Φ-direction on a θ-surface. All these results are as would be anticipated; and they will here be assumed without proof.

The equations[2] which then remain to be solved are

$$\left.\begin{aligned} dp/d\theta + 2p\cot\theta &= 0, \\ (1/r)(dv/d\theta - v\cot\theta) &= p\varphi, \end{aligned}\right\} \qquad (1)$$

where p = the shearing stress in the Φ-direction on a θ-surface and v = the circumferential, or Φ-velocity of the liquid.

For the purpose of the analysis it is assumed that the cones are of infinite radius. The remaining boundary conditions are:

[2] See, for example, Love, *Mathematical Theory of Elasticity*, p. 89, 3rd edition, Cambridge University Press. Eq. (1.1) is the form taken by the equation of equilibrium when there is no acceleration and other conditions are as have been assumed here. The left member of Eq. (1.2) is the rate of shear in the medium. So also is the right member, by definition of the fluidity. Cf. Love, p. 56. Love's equations remain unaltered if we interpret strains as rates of strain.

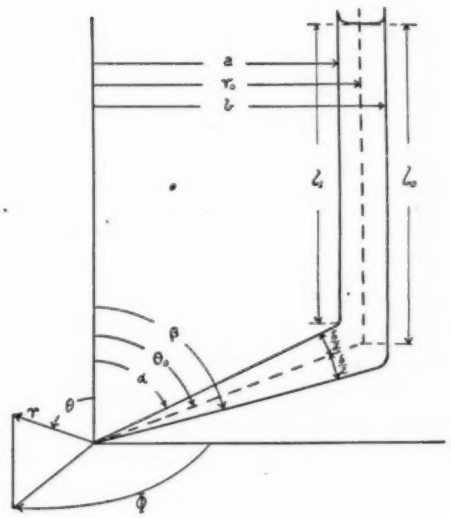

FIG. 1.

$$\left.\begin{aligned} v(r,\alpha)&=0,\\ v(r,\beta)&=r\omega\sin\beta. \end{aligned}\right\} \tag{2}$$

The solution of Eqs. (1) subject to the boundary conditions (2) is

$$\left.\begin{aligned} v&=r\omega\sin\theta\,\frac{\int_\alpha^\theta(\varphi d\theta/\sin^3\theta)}{\int_\alpha^\beta(\varphi d\theta/\sin^3\theta)},\\ p&=\frac{\omega}{\sin^2\theta\int_\alpha^\beta(\varphi d\theta/\sin^3\theta)}. \end{aligned}\right\} \tag{3}$$

We now wish to determine α and β, or their difference, so as to satisfy the condition that the shearing stress and rate of shear between the conical surfaces shall be the same or approximately the same as between the cylindrical surfaces of the viscometer. To be more specific, let us seek to satisfy the condition that the shearing stress between the cones at the mean value of θ shall equal S, the mean shearing stress between the cylinders, or

$$p_0=S. \tag{4}$$

In an analysis of the cylindrical viscometer[3] it is shown that, except for higher terms in ϵ which may be neglected in the present analysis, the fluidity at the mean stress, φ_0, is given by

$$\varphi_0=\omega/\epsilon S, \tag{5}$$

in which $\epsilon=(b^2-a^2)/(b^2+a^2)$.

Then from Eqs. (3.2), (4) and (5) we have

$$\frac{\omega}{\sin^2\theta_0\int_\alpha^\beta(\varphi d\theta/\sin^3\theta)}=\frac{\omega}{\epsilon\varphi_0}. \tag{6}$$

Furthermore, as a consequence of (4) we must have $\varphi(\theta_0)=\varphi_0$. If ϵ is small, as it is in a well-designed viscometer, the angle $(\beta-\alpha)$ will likewise be small. Hence, by Eq. (3.2), the range in p will be small. Therefore, even if φ is not constant, the range in φ will be small unless there is a very unusual discontinuity in the fluidity-stress curve of the liquid. As a valid approximation, the φ under the integral in Eq. (6) may therefore be set equal to the constant φ_0. We then obtain:

$$\epsilon=\sin^2\theta_0\int_\alpha^\beta\frac{d\theta}{\sin^3\theta}. \tag{7}$$

If we now set:

$$\delta/2=\beta-\theta_0=\theta_0-\alpha, \tag{8}$$

the integral in Eq. (7) can be developed as a power series in δ (expressed in radians), and by reversion we finally obtain:

$$\delta=\epsilon\sin\theta_0+\epsilon^3(\tfrac{3}{8}\sin^3\theta_0-\tfrac{1}{2}\sin\theta_0)+\cdots. \tag{9}$$

θ_0 being chosen arbitrarily, Eq. (9) then determines δ, the angular separation of the cones, so as to satisfy the condition that the shearing stress and rate of shear should have, to the first approximation, the same values in the conical and in the cylindrical regions of the viscometer.

Our next step is to calculate the torque resulting from the integrated shearing stress acting on a conical surface in the viscometer. If we consider the situation at the corner, where the cones and cylinders meet, we conclude that the actual torque would be slightly greater than what we would calculate for the upper cone and slightly less than what we would calculate for the lower cone. A similar statement applies to the sides of the two cylinders, which are of slightly different length. Therefore, without attempting to analyze further the corner effects,

[3] M. Mooney, J. Rheology **2**, 210 (1931).

we calculate the torque acting across the surfaces where the stress has the mean value S. In the cylindrical region, this surface has the radius r_0, given by:

$$r_0^2 = 2a^2b^2/(a^2+b^2). \tag{10}$$

In the conical region the surface is defined by $\theta = \theta_0 = (\alpha+\beta)/2$, as previously indicated.

The torque on the bottom is then given by:

$$T_b = \int_0^{r_0/\sin\theta_0} 2\pi r^2 p_0 \sin^2\theta_0 dr. \tag{11}$$

Integrating and using Eqs. (4) and (5), we obtain,

$$T_b = \frac{4\pi\omega r_0 a^2 b^2}{3\varphi_0 \sin\theta_0 (b^2-a^2)}. \tag{12}$$

The torque acting on the cylindrical surface is, in our present notation,

$$T_s = \frac{4\pi l_0 \omega a^2 b^2}{\varphi_0 (b^2-a^2)}, \tag{13}$$

where l_0 is the effective length of the cylindrical region, measured from the upper liquid level to the intersection of the cylinder of radius r_0 with the cone $\theta = \theta_0$. l_0, the immersed length of the inner cylinder, is given in terms of l_1 by the relationship

$$l_0 - l_1 = a\cot\alpha - r_0\cot\theta_0, \tag{14}$$

which can be reduced by approximations to the form

$$l_0 = l_1 + \frac{b-a}{2\sin\theta_0}(1-\cos\theta_0). \tag{15}$$

By adding the members of Eqs. (12) and (13) an equation for the total torque, T, is obtained, which can be solved for φ_0, the mean fluidity, giving:

$$\varphi_0 = \frac{\omega}{T}\cdot\frac{4\pi l_0 a^2 b^2}{b^2-a^2}\left(1+\frac{r_0}{3l_0\sin\theta_0}\right). \tag{16}$$

An explicit formula for the mean shearing stress, S, can likewise be obtained by suitable algebraic manipulation of the previous equations.

$$S = \frac{T}{2\pi r_0^2 l_0 (1+r_0/3l_0\sin\theta_0)}. \tag{17}$$

Description of the Instrument

A conicylindrical viscometer is shown in Fig. 2, built primarily for use with rubber latex. The outer cylinder, 1, is the stator. The inner cylinder, 2, is the rotor, and is driven by a pair of equal weights producing a torque in the same direction. Only one of the weights, 3, is shown in the drawing, suspended by a silk thread over the pulley 4. The stator is surrounded by an asbestos-lagged water jacket, 5. The jacket is provided with a thermometer hole and inlet and outlet for circulating water, which are not shown. The rotor turns on a jewel bearing, 6, at the bottom and has a steel conical bearing, 7, at the top. The trough, 8, surrounding the stator at the top, is to catch the overflow liquid from the viscometer when the rotor is lowered into place. The cover, 9, formed in two halves, serves to prevent evaporation and skin formation on the upper surface of the liquid.

The radii of the cylindrical sections of rotor and stator are, respectively, 2.1 cm and 2.0 cm, leaving a clearance of 1 mm. The bottom of the stator is flat. The bottom of the rotor is a cone of half-angle 87° 2′, as required by Eq. (9). The inside corner of the stator where bottom and side meet is rounded slightly to facilitate cleaning. Since the clearance between the bottom surface of the rotor and stator is important, a metal ring is provided which has the form of the space between the two bottom surfaces; and

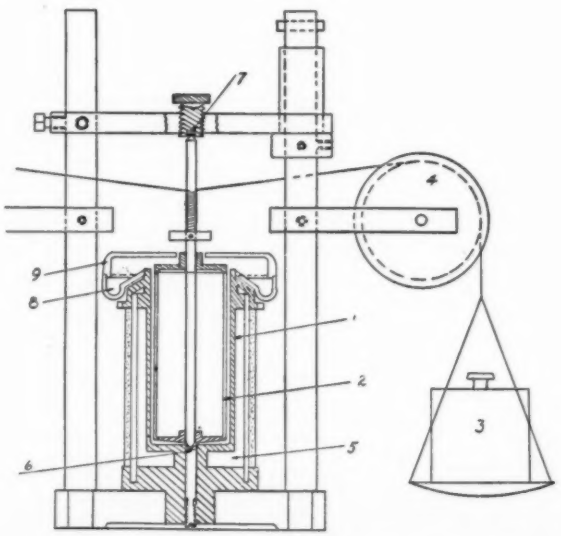

Fig. 2. Details of the conicylindrical viscometer.

the height of the lower bearing is adjusted by means of a screw while the ring spacer is in place. Metal parts of the viscometer are made of stainless steel.

All moving parts of the viscometer are made as light as possible, consistent with appropriate strength. The rotor is hollow and weighs 45 g when immersed in water up to the working level. The pulleys are of fiber and turn on steel conical bearings. The most satisfactory thread found for supporting the driving weights is No. 60 silk tatting thread.

Calibration

Three instruments of the design shown in Fig. 2 were calibrated at the same time with the same series of glycerine solutions. These solutions were made up from Armour and Company "Chemically Pure," U.S.P. glycerine and the specific gravities determined at 25° by pycnometer. The percentage glycerine and viscosities were then obtained by interpolation from Sheeley's tables.[4]

The temperature in the water jacket of the viscometer during calibration was determined by a thermometer graduated to 0.2°C, which was checked against a Bureau of Standards thermometer. The instrument constant k was defined by the equation:

$$\eta = 1/\varphi_0 = kT/\omega, \tag{18}$$

in which η is the mean viscosity.

Eliminating $\varphi_0 T/\omega$ between Eqs. (16) and (18), we express k theoretically in terms of the dimensions of the instrument:

$$k = \frac{b^2 - a^2}{4\pi l_0 a^2 b^2 (1 + r_0/3l_0 \sin\theta_0)}. \tag{19}$$

Table I, in columns 5, 6 and 7, gives the experimental values for k calculated by Eq. (18) from data obtained with a series of different glycerine solutions, and also, in the last row, the theoretical values calculated by Eq. (19). The theoretical values are slightly different for different instruments because of small differences in the dimensions of the finished instruments. Each experimental value of k shown is the average of either three or four values obtained with different driving torques. The variation of these individual values from the mean was about 0.5 percent. The fact that the checks obtained on the same solution with different instruments are better than those obtained with different solutions on the same instrument indicates that the variations are largely due to errors in the assumed viscosities of the solutions rather than in the data obtained with the viscometers.

Table I. *Experimental and theoretical values of instrument constant k.*

Solution	% Glycerine	Viscosity-Poises 20.0°C	22.5°C	Values of $k \times 10^4$ Instrument No. 1	No. 2	No. 3
A	94.65	5.03	4.18	1.79	1.98	1.81
B	92.37	3.50	2.88	1.86	1.95	1.86
C	90.24	2.44	2.02	1.96	2.06	2.02
D	80.50	0.656	0.557	1.92	1.98	1.94
E	69.12	0.213	0.189	1.89	1.90	1.88
Experimental average omitting *A*				1.91	1.96	1.92
Theoretical				1.93	1.94	1.90

In the investigation of the friction in the instrument when in actual operation, the most reliable test was given by the stress-rate of shear curve, shown in Fig. 3, when the instrument was filled with water. The stress intercept shown is equivalent to a driving load of about 0.2 gram. It will be noticed that at higher loads turbulent flow sets in. For this reason it was not possible to obtain reliable determinations of the friction

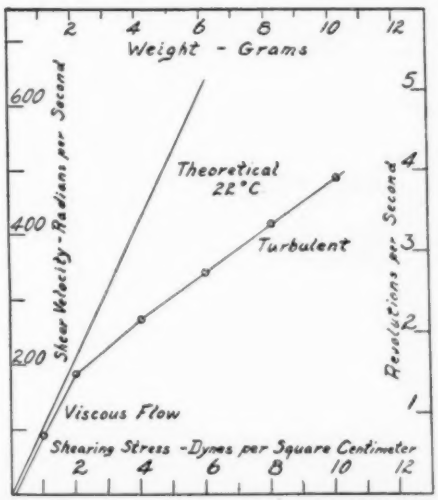

Fig. 3. Measurements with water in the conicylindrical viscometer.

[4] M. L. Sheeley, Ind. Eng. Chem. **24**, 1060 (1932).

at high loads. With the two driving loads opposing each other and with only a drop of liquid in the viscometer on the lower bearing, the friction was 2.3 grams at zero load and increased about 0.5 g per 100 g total load. The actual friction in the instrument while in use would be less than this because of the bouyant action of the liquid on the rotor and because the driving thread tends to bind more when the loads are opposing each other.

The conicylindrical viscometer in its present form is thus shown to be an absolute instrument of considerable precision in measuring viscosities of 0.05 poise or more; and in this range it has also been found more convenient to use than the capillary viscometer previously used for the same materials.

Summary

A new rotating cylinder viscometer is described in which the bottom surfaces of the two cylinders are cones of slightly different angle. The hydrodynamical theory of the conical region is developed, and a formula is given for the proper angular separation of the conical surfaces to produce the same rate of shear between the cones as between the cylindrical sides. The theoretical relation between viscosity, applied torque and rate of rotation is checked experimentally by measurements with glycerine solutions of known viscosities.

Notation

a = radius of inner cylinder,
b = radius of outer cylinder,
g = gravitational acceleration,
k = instrument constant,
$= \eta\omega/T$,
l_1 = immersed length of inner cylinder,
l_0 = effective mean length of inner and outer cylinders,
$= l_1 + \frac{b-a}{2} \cdot \frac{1-\cos\theta_0}{\sin\theta_0}$,
p = shearing stress in the conical region,
p_0 = shearing stress at $\theta = \theta_0$,
r = radius vector,
r_0 = effective mean radius of inner and outer cylinders,
$= [2a^2b^2/(a^2+b^2)]^{\frac{1}{2}}$,
S = mean shearing stress at the inner and outer cylinders,
$= T_c/2\pi l_0 r_0^2$,
T = total torque,
$= T_s + T_b$,
T_s = torque on side (cylindrical) surface,
T_b = torque on bottom (conical) surface,
v = velocity of the liquid.
α = angle of the inner cone,
β = angle of the outer cone,
$\delta = \beta - \alpha$ (in radians),
$\epsilon = (b^2-a^2)/(b^2+a^2)$,
η = mean viscosity of the liquid,
θ = colatitude angle of spherical coordinate system,
θ_0 = mean angle of inner and outer cones,
$= (\alpha+\beta)/2$,
φ = fluidity of the liquid,
$= \frac{\text{rate of shear}}{\text{shearing stress}}$,
φ_0 = fluidity at $\theta = \theta_0$, or at $r = r_0$,
Φ = longitude angle of spherical coordinate system,
ω = angular velocity of rotor (in radians/sec.).

Glossary of Important Equations

$$\varphi_0 = \frac{\omega}{T} \cdot \frac{4\pi l_0 a^2 b^2}{b^2-a^2}\left(1 + \frac{r_0}{3l_0 \sin\theta_0}\right). \tag{16}$$

$$S = \frac{T}{2\pi r_0^2 l_0\left(1 + \frac{r_0}{3l_0 \sin\theta_0}\right)}. \tag{17}$$

$$l_0 = l_1 + \frac{b-a}{2} \cdot \frac{1-\cos\theta_0}{\sin\theta_0}. \tag{15}$$

$$\delta = \epsilon \sin\theta_0 + \epsilon^3\left(\tfrac{3}{8}\sin^3\theta_0 - \tfrac{1}{2}\sin\theta_0\right). \tag{9}$$

The Flow Characteristics of Sewage Sludge and Other Thick Materials*

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(Received July 27, 1934)

FOR the operation of clarifying plants, there was need for data on the pressure loss of sewage sludge in pipes, to form a basis for calculating the economical pumping of sludge to long distances.

The chief difficulty lay in the greatly changing composition of such a sludge and the different effects which the separate ingredients exert on its flow characteristics. Therefore a purely mechanical investigation, no matter how carefully and thoroughly undertaken, as for example in Chicago, Baltimore and Syracuse,[12] could not lead to a satisfactory result. The author sought to determine the separate relations and correlations by numerous observations, and thus came to results which are of significance not only for the sanitary engineer but also for rheologic research and for industry, insofar as they have to do with the mixing and pumping of thick materials.

The tests were mostly carried out at the Stuttgart clarifying plant, and also partly at Nuremberg. The best results were obtained by flow tests in which sludge from the fermentation chamber of an Imhoff tank was discharged into a well until it reached the level of the surface of the settling basin (Fig. 1). After applying various corrections, useful curves were obtained which showed the relation between the average velocity of flow in the pipe and the loss of head, from the highest value at the start of the test (velocity $v=1$–3 m/sec., lost head $J=6$ percent) until equilibrium was reached ($v=0$, $J=0$). The special losses (at entrance, elbows, etc.) could be eliminated by suitable arrangement and determined separately. Other tests were made on straight pipe (20–40 m long) with constant head and different diameters; the distribution of velocities on a section could be observed in open channels, in straight stretches, on curves, at contractions and enlargements of section.

Finally measurements with the Kaempf viscometer[5, 7] at any concentration and temperature made possible the final explanation of relationships which could not be determined by the large scale tests.

Only the rheologically important results will be given here. Sewage sludge is a mixture of water, solutions and colloids, with coarse material up to a few centimeters in diameter according to the free width in the racks before the clarifying plant. Of the solid parts of fresh sludge, 20–30 percent are of inorganic nature (fine sand and ashes; coarse sand is mostly separated out in a sand trap before the clarifying plant). The rest is organic refuse from housekeeping and factories, as well as fecal matter. The organic constituents have the characteristic of adsorbing a considerable amount of water, i.e., micelles are formed with liquid envelopes. This causes the sludge to become viscid and slimy. During the fermentation which takes place under the action of bacteria, the colloids are first built up with their great surfaces, by which a large amount of water is set free. The coarse lumps fall apart into small pieces, go partly into solution or into colloidal form, and then likewise disintegrate. The organic material, during the fermentation, undergoes not only a mechanical and chemical transformation, but also a loss of material, due to the release of water and of gases (mainly CO_2 and CH_4; all together about 5–800 liters of gas per kg of organic material). By the decrease in the organic part of the solid material of the sludge, the viscosity is decreased, but this increases the effect of the inorganic, mainly granular, constituents. As the water content of such a sludge decreases, it finally changes to an earthy mass.

The derivation of an equation of flow for sludge from the limiting conditions is impossible, for such an equation cannot be satisfactorily derived either for water (apart from laminar flow) nor for dry earth.

In the investigation of the flow characteristics of plastic materials, four ingredients must be considered, each of which obeys different laws.

* Extract from a paper by the author, under the same title, which was published by R. Oldenbourg, Munich, as Series II, No. 14, Beihefte zum Gesundheits-Ingenieur. Translation by W. H. Herschel.

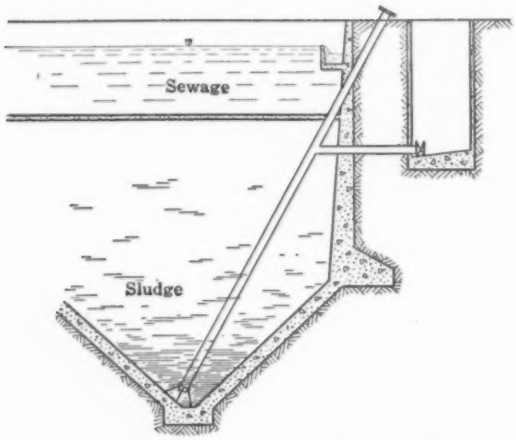

FIG. 1. Arrangement of experimental plant.

1. The free dispersion medium; it is in general a simple viscous liquid with a characteristic resistance, its viscosity μ.

2. The bound dispersion medium, forming with the lyophile kernel which it covers, a slimy mass; here there are added adsorption and capillary forces which resist shearing and cause an increase in viscosity.

3. Small lyophobe particles which hardly affect the fluidity of the system when present in small amounts, but only when numerous enough for the separate particles to touch and rub against one another, they cause a resistance ϑ which does not vanish even at the highest shearing stresses.

4. Coarse objects up to a few centimeters in diameter which take up a considerable part of the pipe section and prevent the formation of a normal velocity profile.

If we take up the quantitative consideration of the flow characteristics we must first be clear about the effect of the fourth constituent. In fermented sludge all the large particles of the fourth constituent occur only in small amounts, and normally in fresh sludge there is so much water present that here also they do not play an important part. We can therefore leave them out of consideration, or include them in the very large tolerance required from the variations in composition of the sludge.

The action of the free water remains fixed; it follows Newton's law $\tau = \mu dv/dr$. With constituent 3 it is to be observed that coarse lyophobe particles, or those which do not adsorb water, cannot be regularly distributed and carried along in laminar flow, since they sink on account of their greater weight, and at most are rolled along the bottom of the pipe. Only in a medium with structural viscosity can lyophobe particles be carried along at any elevation. However we also have the so-called "pseudo-laminar" flow. As above stated, a noticeable effect on the flow characteristics takes place at a concentration such that capillary effects are possible in consequence of the small distances between particles, or the solid particles rub on one another. This friction is nearly independent of the velocity (but not of the pressure) i.e., τ = constant. To be sure, when the solid particles exceed a certain size, additional resistances are caused from the fact that the particles are not spherical and become wedged in the spaces between other particles; this is the more so the longer time they have, or the less the velocity. We thus have an increase in resistance as the velocity decreases, which has nothing to do with the resistance to slip of the solid particles.

It is similar with the bound water. Here also the resistance decreases as the velocity increases. In a state of rest the mass held together by bound water is essentially elastic, and then τ = transverse modulus of elasticity $\times$ shearing stress s. This resistence is overcome when motion starts, and at high velocities is entirely destroyed. It is not to be assumed that the water held in the capillaries acts essentially differently from the bound water in the solvation envelopes. This causes the difficulty in experimenting that the resistance for a given velocity has a different value according to whether it is reached by acceleration from a lower velocity, or by retardation of a higher velocity. In the first case it is greater than it should be, in the second case, smaller; for the destruction of the structure requires time, and so does building it up again. It is also not to be forgotten that the sludge is constantly changing in consequence of biological and chemical processes as well as by mechanical stirring.

The flow characteristics will vary according to the proportions in which the four components are present in the entire mass.

Corresponding to the definition viscosity $\mu = 1/\text{fluidity}$, φ for simple viscous liquids, ac-

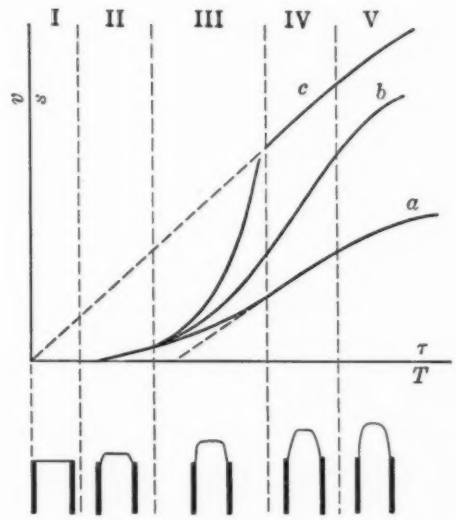

FIG. 2. The five types of flow of plastic bodies. Velocity distribution over bore of tubes. v and τ are velocity and gradient in the tube. s and T are the shear and torque in the rotation viscometer. The lower part of figure shows variation in velocity across the pipe section.

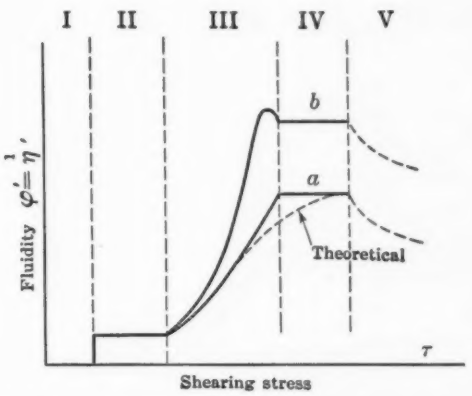

FIG. 3. Mobility $\varphi' = 1/\mu$ plotted against shearing stress τ.

cording to Bingham we should have for the resistance of a plastic material, $\mu' = 1/\text{mobility}$, φ'. Since $v = Q/F$ is the *average* velocity in the section of the pipe, φ' should be the reciprocal value of the *average* resistance of the material in the pipe. (Q = quantity discharged in unit time; F = section of pipe.)

With a shearing stress τ less than a certain τ_0 in consequence of the friction or interlocking of the solid particles, and also when the jelly strength is high enough also on this account, no flow will take place or at most an elastic deformation. (Regime I of Figs. 2 and 3.) As τ increases, a layer is sheared off in the plane of highest stress, that is, near the walls of a pipe, or in the case of a rotation viscometer, near the surface of the rotating body or of the inner cylinder. The mass then moves like a plug through the pipe, without further breakdown in structure (regime II in Figs. 2 and 3).[13, 14] In the rotation viscometer the inner cylinder slips along a plane of shear in the otherwise undisturbed sludge. In this case therefore, there is the shearing of one layer of liquid between two solid bodies. When v increases, the resistance to flow remains constant for a while (dv/dJ = constant). Finally, however, the shearing stress transferred from the plane of shear exceeds the resistance of the adjacent layer, and so on; more and more layers (in a pipe, concentric rings) come into motion relative to the core remaining fixed at the axis of the pipe, i.e., a core of decreasing size runs more and more ahead of the surrounding layers. This core, really a rod, considered as a whole, could never, theoretically, lose its solidity entirely, since $\tau = 0$ at the axis of the pipe, but it is carried along. Next regime III of the flow curve shows a gradual increase in mobility and the curve must approach asymptotically to an inclined straight line; as an actual fact it coincides with this above a certain point. (Fig. 2, regime IV, curve *a*). The straight line of regime IV is applicable practically and theoretically to the rotation viscometer, since between two concentric cylinders having relative motion, the shearing stress or the velocity gradient never becomes zero. The intersection of the straight line extrapolated backwards, with the axis of abscissas, gives the rigidity (Bingham's "yield value") of the material; its dimensions are those of a stress, g/cm².

If the sludge has no third constituent, no solid lyophobe component, which has a certain minimum resistance, but also no remaining structure in the lyophile parts which is not affected by the shearing, if therefore the sludge has only an initial jelly strength which can be completely destroyed, then in regime IV of the flow curve *b*, it will be represented by a straight line which passes through the origin when extrapolated backwards, which corresponds to a true Poiseuille flow.

Finally turbulence begins in regime V, within

which, with increasing distance from the critical velocity, the characteristic differences of the 4 flow constituents disappear. (Concerning the velocity distribution in pipes in turbulent flow.)[6, 8]

Naturally between curves IV*a* and IV*b* there is the possibility of curves like IV*c* which, without any intermediate straight portion, go over imperceptibly into the curve of turbulent flow, concave downward.

Fig. 3 is obtained if, instead of the values v and J, the shearing stress and mobility are plotted, as for example they are obtained in the rotation viscometer. Since the mobility φ' is a function—to be sure different for each regime of flow—of τ and v is a multiple of φ', the curves of Fig. 2 may be regarded as integral curves of Fig. 3. The peculiar maximum value of φ' to be observed in Fig. 3, curve *b*, which corresponds to the change in curvature in Fig. 2, curve *b*, is easily explained. Since a pipe not completely full (about 90 percent) will carry more water than when entirely full, so also a plastic mass, which has a still unsheared core around the axis of the pipe, may have a lower resistance than when the parabolic velocity profile has been formed across the entire pipe section. For with the same rate of flow, in the first case the surfaces of the layers slipping past one another are essentially smaller, while the velocity gradient is only slightly larger than in the second case.

The curves, sketched above, of Figs. 2 and 3, are to a certain extent ideal. Only very seldom is it possible to distinguish between all five regimes and recognize them. With a not homogeneous material, such as sewage sludge, they will generally blend more or less. If turbulence occurs early, regime IV may be left out completely, with increasing water content regime II becomes III, and also regime I may completely disappear (Fig. 4).

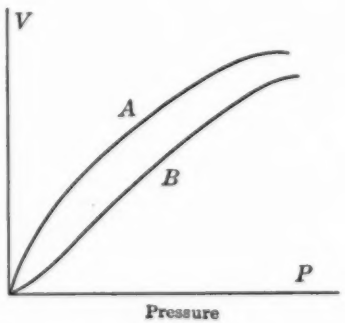

FIG. 4. V plotted against pressure P (after Ostwald). *A* is for mercury sulpho salicylic acid sol. *B* is for a 1 percent gelatine sol.

Until now it has been tacitly assumed that only such a sludge would be considered as contained enough water so that pumping it through pipe lines would come under consideration. With an air-dry, fermented sludge, the constituent No. 1 (free water) and No. 2 (slimy material) are so unimportant in comparison with No. 3 (lyophobe particles) that, in consequence of the large friction of these solid particles, flow under pressure through the pipes is no longer possible. For when lubrication is lacking the friction of solid bodies increases with increased pressure (when pressed together the surfaces of contact are increased by elastic yielding) until finally pressure arches are formed in the pipe. These arches are first solidified by further increase in pressure, and are destroyed only at much higher pressures. Not until the sludge is completely dried (cured) could conveying through pipes be again considered, but then in powdered form transported by air, i.e. with air as the vehicle.

From what has been said there is no prospect of setting up a single general equation, to cover all the variations and the separate regimes of flow of sewage sludge or of plastic materials in general. It is therefore necessary to start with data tables giving supplements for the most varied effects, such as are available for draining land, in the field of cultivation. A diagram according to the available experimental data is shown in Fig. 5. There is still need of the cooperation of colleagues to determine the coefficients more exactly and to carry the work further until it suffices for the manifold relations of practice.

Now if no general equation of flow can be obtained, there may yet be found a suitable formula for a restricted field. Reiner[9] derived such a one in seeking a general law. In the regimes of flow III and IV, which with different kinds of sludge generally occur between 80 and 88 percent water content, it may be used with good approximation to convert to other ϕ, v and J. It is derived from the relation $\tau = \vartheta + \mu dv/dr$ and reads,

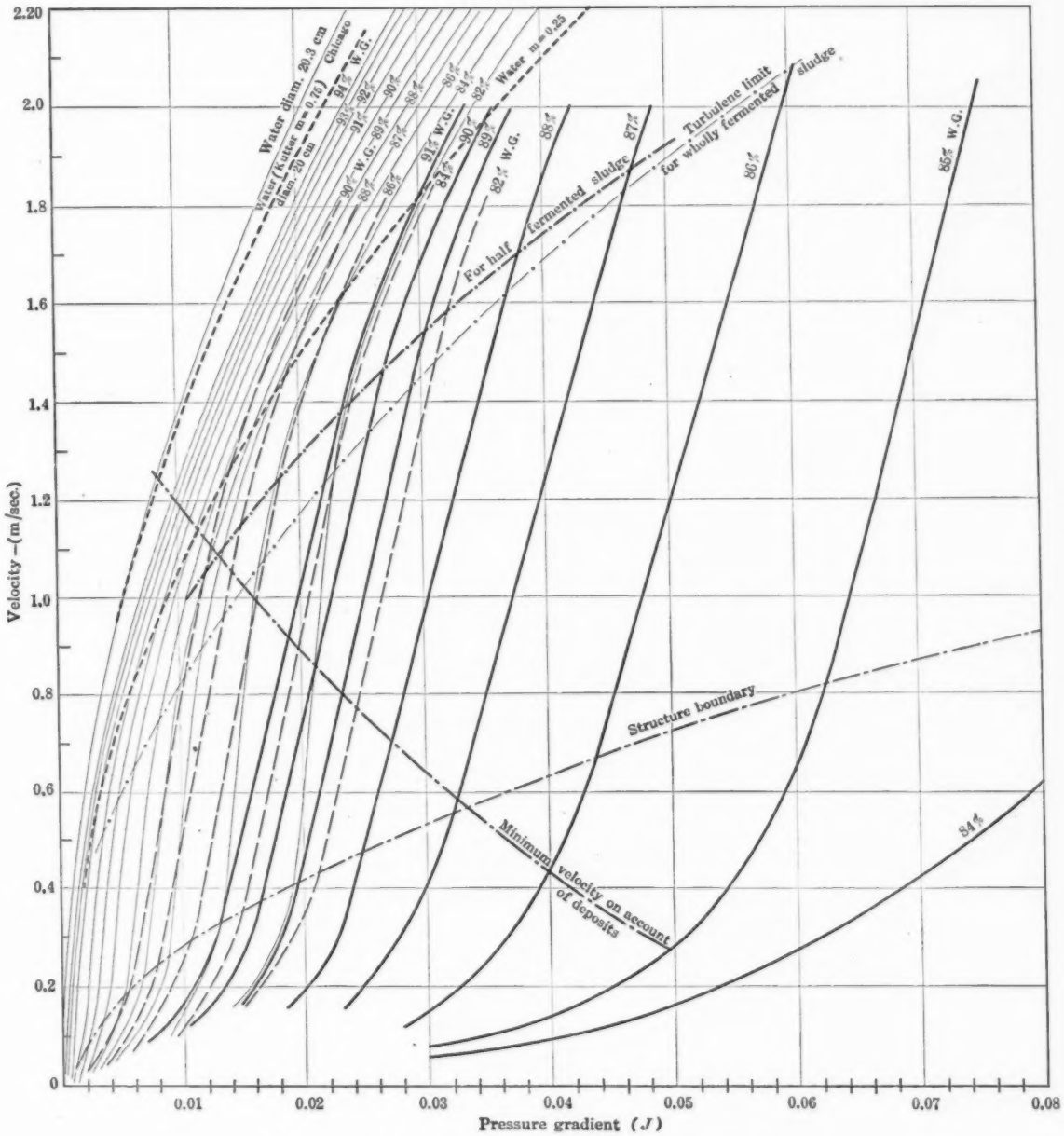

FIG. 5. Pressure loss of sewage sludge in pipes 20 cm in diameter.

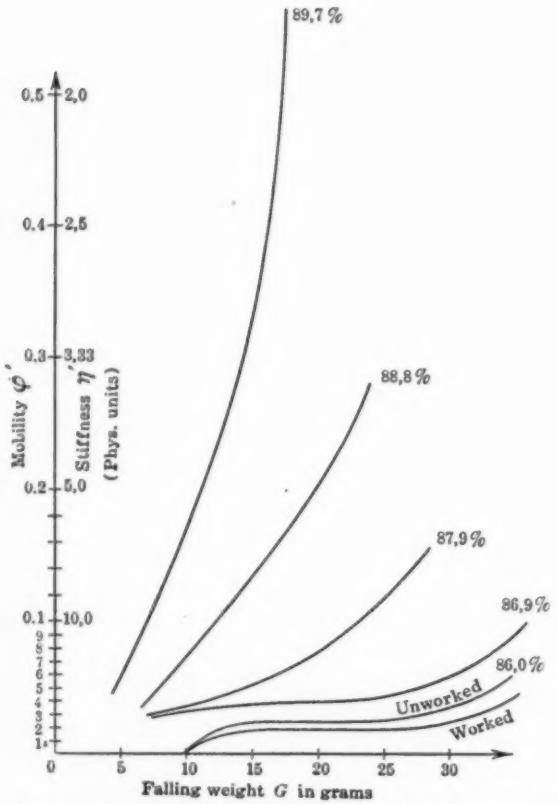

FIG. 6. Sewage sludge from a leather factory at 20°C (viscometer tests). Mobility φ' and stiffness μ' (physical units) plotted against falling weight G in grams. The two lowest graphs are marked "unworked" and "worked," i.e., unstirred or stirred before testing.

$$v_{m/sec.} = \frac{r^2 J\gamma}{800\mu}\left[1 - \frac{2.667\vartheta}{J\gamma r} + 5.33\left(\frac{\vartheta}{J\gamma r}\right)^4\right]. \quad (1)$$

Here r is to be taken in cm and μ in the technical unit g·sec./cm²; ϑ has the unit g/cm² and γ is g/cm³. Without the quantity in brackets we have the Poiseuille equation, which is thus a special case of this general equation. The third term in the brackets can be neglected on account of its small value above a limiting "structure." The curve therefore goes over to a straight line. In the curves calculated from the above equation, their asymptotes are parallel to the Poiseuille lines with the same μ. In the regime where the third term can be neglected, the equation may be written more simply,

$$v = \frac{r^2 J\gamma}{800\mu} - \frac{2.667 r\vartheta}{800\mu}. \quad (2)$$

The yield value f, or the measure of the horizontal parallel displacement of the straight lines of Eq. (2), as compared with the Poiseuille straight lines, $v = r^2 J\gamma/800\mu$, becomes $f = J_{v=0} = 2.667\vartheta/r\gamma$. Two known points suffice for conversion in the IVth regime of flow.

With increasing fermentation, naturally with the same water content, μ decreases and ϑ increases. (See Fig. 5 with the steeper curves for the completely fermented summer sludge as compared with the flatter ones for the only half fermented sludge of low winter temperatures.)

For comparison with the experimental results with sewage sludges reference will be made to publications which treat of other plastic materials and show the same results. Scott Blair[12] shows the flow curve of a loam paste which shows very beautifully the above mentioned regimes of flow. For loam, as a mixture of lyophile clay and lyophobe sand, is very similar to sewage sludge. Further the curves for zinc sulphide in α-bromonaphthalene[1] show an agreement with Fig. 5.

As an especially instructive example of the results obtained with the Kaempf viscometer, curves are shown in Fig. 6, which were obtained in tests of sewage sludge from a leather factory. Noteworthy is the evident occurrence of the II regime of flow (see Fig. 3). Since the thixotropic stiffening of the leather sludge was not great and the stiffening time was relatively long, the separate values show only slight deviations on repetition. Further details are given in the paper of the author above referred to.

In addition to the direct significance which the flow curves obtained have for the conveyance of sewage sludge, advantages are to be expected from applying the theoretical results to other plastic materials. In all industries where plastic materials are prepared, mixed, pumped and worked, flow curves should be prepared for the material in question, and it will surely be seen in many cases that the efficiency may be considerably increased by changing the velocity of mixing or of flow. Especially in the IV regime of flow a certain increase in driving force corresponds to quite a considerable increase in output. If a material is thixotropic, the increase in efficiency by increase in motor capacity is even more striking.

In this connection may be remembered the use of grout, the preparation of road foundations

with tar or bitumen, pumping paper stock and molasses, and the wet transportation of any kind of refuse.

In summary it may be said, if any kind of thick material is to be investigated as regards its flow characteristics, a clear distinction must be made between different materials:

1. Clean or slightly soiled liquids. It is first to be determined whether or not the flow is turbulent at the expected velocity. In turbulent flow the well known formulas for water are to be applied with suitably changed coefficients; the roughness of the walls is to be taken into consideration.

If laminar flow is to be expected, Poiseuille's law applies. Only the viscosity has to be determined; a moderate roughness of the walls plays no part.

With increasing contamination of the liquid, the validity of the above methods of calculation disappears and it is to be determined whether and to what extent the suspended solid particles attract and bind the liquid to them (lyophile) or not (lyophobe).

2. With increasing content of lyophile particles, the viscosity μ increases very rapidly and thixotropic phenomena are also to be expected. The critical velocity increases, below it there may be a true laminar regime (a straight velocity-pressure drop line through the origin). At lower velocities, greater resistance, and under certain circumstances, a yield value may appear.

3. Increasing addition of lyophobe material does not necessarily have a large effect on the viscosity, so long as it does not become so great that capillary action occurs between the closely packed solid particles. Here appears a flow resistance ϑ. Higher concentrations all have a yield value below which no flow is possible. At high velocities the inner friction can never entirely disappear. There is only over a certain range a pseudolaminar flow, i.e., a flow-pressure drop line which does not pass through the origin. If the amount of the solid lyophobe particles is greater than the amount of liquid, the friction of solid bodies comes to the foreground. Turbulence is no longer possible and friction depends more on the pressure than on the velocity.[4]

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